

**Quality Assurance Project Plan
for the
Great Lakes Water Quality Surveys**

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1.0 PROJECT BACKGROUND

EPA's Great Lakes National Program Office (GLNPO) conducts biannual surveys of water quality within each of the Great Lakes. These surveys are conducted every spring and summer to assist the United States in fulfilling its responsibilities under the Great Lakes Water Quality Agreement.¹ Annex 11 of this agreement requires the U.S. and Canada to conduct surveillance and monitoring activities to:

- (1) Evaluate the degree to which jurisdictional control requirements are being met.
- (2) Assess water quality trends to evaluate the effectiveness of existing control measures and determine if new control measures are needed, evaluate enforcement and management strategies, and identify the need for new research and technology development.
- (3) Identify emerging problems in the Great Lakes Basin Ecosystem.

In response to these requirements, GLNPO has been conducting water quality surveys since 1983. Initially, the surveys focused on chemical eutrophication and whole lake response to changes in phosphorous loadings. Therefore, early monitoring efforts were directed at Lakes Michigan, Erie, and Huron. Lake Superior was excluded from early efforts because it is not affected by eutrophication, and Lake Ontario was not sampled because extensive annual monitoring of that lake was already being implemented by the Canadian government. Lake Superior was added in 1992 to provide EPA with information on a healthy lake and dovetail with environmental monitoring initiatives being pursued under the Environmental Monitoring and Assessment Program (EMAP). Lake Ontario was added later to supplement the Canadian data gathering activities. The scope of the survey parameters has similarly broadened over time and now includes several measures of biological and sediment quality in the lakes.

The Water Quality Surveys are unique in that all five lakes are sampled by one agency, using one vessel and one principal laboratory for each parameter group. Thus inter-lake comparisons based on data collected during the program are not complicated by differences in sampling procedures, interlaboratory differences, or analytical techniques.

2.0 PROJECT DESCRIPTION

GLNPO has primary responsibility within the US for conducting surveillance monitoring of the offshore waters of the Great Lakes. The Water Quality Surveys generally consist of two surveys per year: a Spring Survey and a Summer Survey.² The monitoring effort is focused on whole lake responses to changes in loadings of anthropogenic substances. Generally speaking, change in the water column is best detected in areas of minimal variability and change in sediment quality is best detected in shallower areas where physical and chemical impacts can occur within reasonably short time frames. As a result, sampling activities in the surveys are largely restricted to the relatively homogeneous offshore waters of each lake (for water column measurements) and to the shallow areas of these waters for sediment measurements. To ensure that sampling activities are representative of lake conditions, samples are collected from multiple sites within each lake basin. The number and locations of the sites needed to obtain a representative sampling of each basin was statistically determined using historical data collected during intensive surveys of each lake. Each basin consists of several routine monitoring stations and a 'master station'. The master stations generally represent the deepest area of the basin and are often used to collect supplementary data for other (non-survey) purposes.

¹Great Lakes Water Quality Agreement of 1972, renewed in 1978, amended in 1987.

² The Summer Survey is periodically canceled to allow for dry dock and repairs to the ship.

Sampling activities also are conducted two times per year to capture information about the lakes during different conditions. The spring surveys are designed to collect water quality information during unstratified (isothermal) conditions of the lake, so the survey circuit is planned to move from warmest to coolest waters to ensure that sampling at all sites is conducted before stratification begins. The summer surveys are designed to monitor the quality of each lake during stratified conditions. As a result, the number of depths sampled during the summer is slightly greater than the number of depths sampled during the spring surveys.

Survey activities are conducted onboard EPA's *R/V Lake Guardian*, a former offshore oil field supply vessel built by Halter Marine, Moss Point, MS, in 1981. Ship dimensions are: 180' length, 40' beam, 11' draft, and 850 displaced tonnage. Propulsion is twin screws enclosed in Kort nozzles and driven by 1200 hp Caterpillar diesel engines. Cruising speed is 11 knots; range is 6,000 miles. Sampling activities onboard the Lake Guardian are primarily implemented through the use of:

- A Rosette sampling device deployed from the ship to collect samples for a variety of nutrients, physical parameters, and biological parameters
- Tow nets used to collect zooplankton samples, and
- A Ponar grab sampling device used to collect sediment samples for benthic organisms and chemical measurements.

Most of the survey measurements are made on board the ship, either on the bridge or deck (e.g., meteorological measurements such as wind speed and direction, wave height and direction, air temperature, etc.), by the conductivity/temperature/depth (CTD) probe attached to the Rosette, or in the on-ship laboratory (e.g., turbidity, conductivity, pH, etc.). The remaining measurements are made by GLNPO's Great Lakes Analytical Services (GLAS) contractor and a biology grantee in land-based laboratory facilities. Table 2-1 provides a detailed list of all parameters monitored during the surveys.

The surveys are timed to occur at roughly the same time each year, with minimal variations allowed for weather conditions (e.g., ice dispersal, storms, etc.) and other scheduling constraints such as the availability of services while in port.

- The Spring Survey generally lasts 40 days, with the first 25 days covering a circuit that runs from Milwaukee, WI through Lakes Michigan, Huron, Erie, and Ontario, returning through Lake Erie to Bay City, MI. Lake Superior is sampled last, after ice has sufficiently dispersed. The Lake Superior sampling period, including transit, generally lasts approximately 15 days.
- The Summer Survey generally takes 35 days beginning in the first week of August; it covers a transit from Bay City, MI through Lakes Erie and Ontario, and returning through Lakes Erie, Huron, and Michigan and then transiting to Lake Superior.

Table 2-1. List of Parameters Monitored in the Great Lakes Water Quality Surveys

Parameter Class	Parameter	Sampling Device/Measurement Location
Nutrients	Nitrate plus Nitrite Nitrogen (NO ₂ /NO ₃) Particulate Organic Carbon (POC) Total Phosphorus Total Dissolved Phosphorus (TDP) Particulate Nitrogen Chloride Particulate Phosphorus Reactive Silica	Rosette/land-based lab
Physical Measurements	Aesthetics Optical Transmittance Air temperature Water Temperature Turbidity Wind Speed Wind Direction Specific Conductivity Alkalinity pH Water Clarity Total Suspended Solids Wave Height Dissolved Oxygen Site Location	Observation/Bridge SeaBird CTD Digital Thermometer/Bridge SeaBird Rosette/Board Danforth/Bridge Danforth/Bridge Rosette/Board Rosette/Board Rosette/Board Secchi Disk/Deck Rosette/land-based lab Observation/Bridge Rosette/Board and SeaBird CTD probe Digital GPS/Bridge
Biological Indicators	Phytoplankton Zooplankton Benthic Invertebrates Chlorophyll a	Rosette/land-based lab Tow nets/land-based lab Ponar Grab/land-based lab Rosette/land-based lab

* Dissolved organic carbon (DOC) also is determined when hydrophobic organic compounds are included in special studies.

In addition to the general Water Quality Monitoring Surveys described above, GLNPO conducts an intensive dissolved oxygen (DO) survey of Lake Erie each summer. Details of this survey can be found in *Dissolved Oxygen and Temperature Profiles for the Central Basin of Lake Erie Quality Assurance Project Plan*, located in Appendix D of the manual, *Sampling and Analytical Procedures for GLNPO's Open Lake Survey of the Great Lakes*. The United States has made a substantial (approximately \$8 billion) investment in pollution controls to address severe oxygen impairment problems within Lake Erie, and the purpose of GLNPO's annual DO surveys is to determine if these investments are resulting in demonstrable improvements to the lake. To the extent possible, the Lake Erie DO Surveys are timed to coincide with the summer Water Quality Surveys onboard the *R/V Lake Guardian*. Similarly, GLNPO attempts to coordinate its spring and summer survey activities with other organizations, such as EPA Regions 2 and 5, who are involved in Great Lakes research activities. The goal of this coordination is to maximize sampling activities onboard the *R/V Lake Guardian*.

This Quality Assurance Project Plan (QAPP) presents the data quality objectives (DQOs) and measurement quality objectives (MQOs) established for the collection and analysis of environmental samples collected during each Water Quality Survey. This QAPP also describes the roles and responsibilities of the organizations and staff participating in the Surveys and the methods and procedures that will be followed to ensure that Survey DQOs and MQOs are met. This QAPP does *not* address the activities of other projects, such as the Lake Erie DO Survey, that are related to or being conducted concurrently with the Water Quality Surveys. QA requirements and management practices for those studies are described in separate, project-specific QA plans.

This document was prepared in accordance with and contains each of the elements described in the most recent version of EPA's requirements for QAPPs [1]. To improve clarity, the order of certain elements in this QAPP has been modified slightly from the order presented in EPA QA/R-5. For example, the Project Organization section (element "A4" in QA/R-5) comes after the Project Background and Project Description (elements "A5" and "A6" in QA/R-5) in this QAPP.

In accordance with the guidance provided in QA/R-5, this QAPP is considered to be a dynamic document that is subject to change as sample collection and analysis progresses. All changes to procedures described in this QAPP will be reviewed by the GLNPO Quality Assurance Manager, the Environmental Monitoring and Indicators Team Lead, and the appropriate technical leads (e.g., biology, dissolved oxygen, limnology, board chemistry, information management, or bridge measurements), to determine if the changes significantly impact the technical and quality objectives of the project. If changes are deemed to be significant, the QAPP will be revised accordingly.

This QAPP is an appendix to the manual, *Sampling and Analytical Procedures for GLNPO's Open Lake Water Survey* (WQS manual). The procedures and requirements discussed in this QAPP are further described in the WQS manual. The manual is organized into six chapters. **Chapter 1** describes the WQS and includes a Standard Operating Procedure (SOP) for General Shipboard Scientific Operations. This SOP presents information on: 1) roles and responsibilities, 2) the sequence of sampling events, and 3) safety and training. Chapter 1 also includes an SOP for Electronic Field Information Recording. **Chapter 2** provides sampling and analytical procedures for nutrient parameters targeted in the survey. **Chapter 3** provides sampling and analytical procedures for physical parameters including meteorological data and total suspended solids. **Chapter 4** provides sampling and analytical procedures for biological parameters. **Chapter 5** provides analytical procedures for several chemical parameters that are analyzed in the laboratory aboard the *R/V Lake Guardian* ("board chemistry" parameters) including pH, specific conductivity, total alkalinity, turbidity and dissolved oxygen by the Winkler method. **Chapter 6** provides sampling and analytical procedures for nutrients in sediments.

This manual also contains several appendices. **Appendix A** contains maps of the Great Lakes spring and summer survey stations. **Appendix B** contains the quality assurance project plan (QAPP) for the Great Lakes Water Quality Surveys. **Appendix C** contains a staff scheduling form that lists shift dates for proposed and actual GLNPO staff participating in the survey. **Appendix D** contains a QAPP as well as the sampling and analytical procedures used in GLNPO's intensive DO survey of Lake Erie's Central Basin. **Appendix E** contains survey planning forms that must be submitted by researchers requesting use of the *R/V Lake Guardian* for sampling purposes. **Appendix F** contains the self-certification form that all GLNPO staff and contractors/grantees participating in the survey must complete and provide to the GLNPO QA Manager to certify their meeting pre-survey training requirements as specified on the form. **Appendix G** contains the Medical History Questionnaire that is required to be completed and submitted by all personnel that participate in GLNPO's WQS. **Appendix H** contains hard-copy field information recording forms used to document the data generated during the surveys. **Appendix I** contains lists of acceptable field remark, lab remark, and quality control sample identifier codes used in GLNPO's Great Lakes Environmental Database (GLENDa). **Appendix J** contains a user's manual for the GLENDa remote data entry tool. **Appendix K** includes a list of current GLENDa analyte names and codes for environmental parameters being measured. **Appendix L** contains a list of roles and responsibilities for the Chief Scientist, in addition to a list of priorities for each staffing period and a checklist that must be completed by the shift supervisor for each shift of 12 hours and provided to the QA Manager to verify that they met their responsibilities involving ship operations and survey data management. **Appendix M** contains a suggested revision sheet that survey participants should use to document issues, errors, and suggested revisions and clarifications to the manual. **Appendix N** contains a data status tracking sheet to track specific data sets throughout the data verification process and upload to the GLENDa database. **Appendix O** contains a data discrepancy form to initiate a revision to the GLENDa database when errors

are identified. **Appendix P** contains a summary of the sample depth's collected as part of the WQS for all five lakes. Finally, **Appendix Q** contains the station location change form that must be completed and approved by pertinent survey participants to finalize a change to a station location. Earlier revisions of the manual contained: 1) an addendum to the WQS QAPP that provides the information needed to perform the base monitoring program activities on alternate vessels when the *R/V Lake Guardian* is not available (March 2001, Appendix C) and 2) GLNPO's Standard Operating Procedures for Winter Operations (March 2001, Appendix F). These documents are available to support specific projects involving these special circumstances.

The WQS manual also is a dynamic document and in accordance with GLNPO's document and records management policy, a control copy of the manual (and this QAPP therein) is maintained by GLNPO's document control coordinator. The current version of the manual can be obtained from GLNPO's Environmental Monitoring and Indicators Team Lead, the Quality Assurance Manager, and GLNPO's document control coordinator within GLNPO's Policy Coordination and Communications Branch.

3.0 PROJECT ORGANIZATION

The Great Lakes National Program Office (GLNPO) is responsible for overall management of the Water Quality Surveys. GLNPO also is responsible for providing oversight over all scientific activities while onboard ship and for performing many of the sampling and analysis activities onboard ship. GLNPO is supported by a grantee and several contractors, including:

- A grantee organization that provides scientific and technical support in the field and in a land-based laboratory facility for collection and biological analysis of samples.
- A Great Lakes Analytical Services (GLAS) contractor that provides scientific and technical support in the field and in a land-based facility for collection and chemical analysis of samples.
- A Ship Operations contractor responsible for all aspect of ship operations.
- A Chemical Hygiene contractor that provides a Chemical Hygiene Officer for all activities in which scientific operations are being conducted onboard ship.

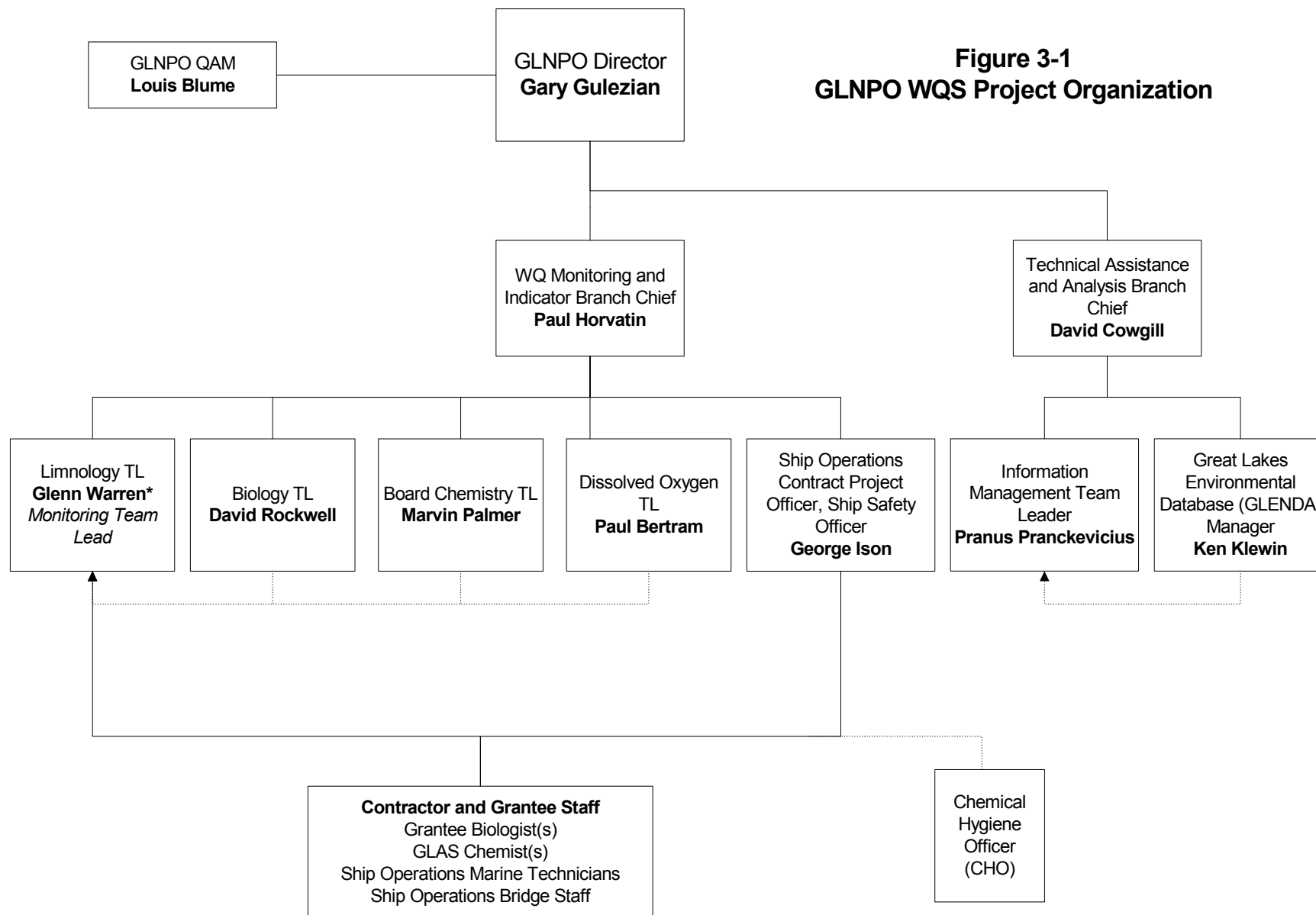
Section 3.1 describes the overall project management and lines of authority within GLNPO and during the water quality surveys. It includes an organization chart illustrating the general organization of GLNPO (Figure 3-1) and detailed descriptions of the roles and responsibilities of GLNPO staff that are involved with management and implementation of the Water Quality Surveys. Section 3.2 describes roles and responsibilities of survey staff while onboard the Lake Guardian. In this section, Table 3-1 illustrates the lines of authority and responsibilities of survey participants while onboard ship. Section 3.3 briefly describes the major roles and responsibilities that must be defined by all grantees and contractors supporting the surveys.

3.1 Survey Project Management

GLNPO is organized into functional teams that specialize in specific areas of interest and expertise for data gathering activities. Each team is comprised of a team lead and staff from GLNPO and where appropriate, other organizations within EPA (such as Region 5, Region 2, etc). Five of the GLNPO teams are directly involved in the Water Quality Surveys:

- 1) Environmental Monitoring and Indicators Team
- 2) Health and Safety team
- 3) Information Management and Data Integration Team
- 4) QA Team
- 5) Management Team

Project management responsibilities within the Water Quality Surveys reflect the emphasis on these four teams, all of whom ultimately report to the director of GLNPO. Specific roles and responsibilities within each of these areas is described below.



**Figure 3-1
GLNPO WQS Project Organization**

TL - Technical Lead

3.1.1 Director of the Great Lakes National Program Office

The GLNPO Director, Gary Gulezian, is responsible for providing financial and staff resources necessary to meet the objectives and implement the requirements described in this QAPP for the Water Quality Surveys. The Director is responsible for establishing GLNPO quality policy and resolving related issues which are identified through the Quality Management Team and survey participants.

3.1.2 QA Manager

The GLNPO QA Manager, Louis Blume, is independent of the Water Quality Surveys project and reports directly to the GLNPO Director. The QA Manager is responsible for assisting the Chief of the Monitoring Indicators and Reporting Branch, the Environmental Monitoring Team Lead, the Technical Leads, and the EPA Project Officer for the Ship Operations Contractor (SOC) with the development and implementation of QAPPs that are consistent with GLNPO's Quality Management Plan and quality system. The QA Manager also is responsible for:

- Concurring with the Technical Leads on all methods and method modifications selected for use in the surveys
- Ensuring that all QA procedures described in this QAPP are followed, reporting any deviations from this QAPP to the Team Leads, Technical Leads, and SOC Project Officer in implementing corrective actions necessary to resolve these deviations
- Conducting periodic Quality System Audits (QSAs) to verify that survey procedures are capable of meeting survey objectives
- Ensuring that all staff participating in the surveys complete a Self-Certification Form that documents they have received all required training
- Ensuring that the Shift supervisors submit a completed Shift Supervisor Checklist (Appendix L), and using information from this checklist to identify roles and responsibilities that require revision or clarification.

The QA Manager reports directly to the GLNPO Director.

3.1.3 Environmental Monitoring and Indicators Staff

The Chief of GLNPO's Monitoring Indicators and Reporting Branch is responsible for providing overall direction concerning all aspects of the Water Quality Surveys. He is supported by an Environmental Monitoring Team Lead and several Technical Leads. Roles and responsibilities for each of these individuals are described below.

3.1.3.1 Monitoring Indicators and Reporting Branch Chief

The Monitoring Indicators and Reporting Branch Chief, Paul Horvatin, reports directly to the GLNPO Director and is responsible for providing overall direction concerning the surveys to the Environmental Monitoring Team Lead and Technical Leads. The Branch Chief also is responsible for:

- Implementing an overall QAPP applicable to all phases of the Water Quality Surveys
- Communicating survey objectives to the Environmental Monitoring Team Lead, and Technical Leads
- Ensuring EPA and contractor resources are available to implement the survey design
- Reviewing and approving all major work products associated with the surveys

- Participating in meetings with the Team Leader, Project Officers, other EPA staff, and staff from other organizations and contractors concerning the surveys
- Working with the GLNPO QA Manager to identify corrective actions necessary to ensure that study objectives are met.

3.1.3.2 Environmental Monitoring Team Lead

The Monitoring Team Leader (Glenn Warren) reports directly to the GLNPO Director, and is responsible for:

- Developing and implementing the scientific aspects of this QAPP
- Reporting to GLNPO's Management Team monthly regarding technical, QA, and resource issues concerning the Water Quality Surveys
- Daily oversight of EPA and contractor staff involved in all survey activities related to sample collection, analysis, and data management for limnology (e.g. nutrients and water chemistry) measurements
- Providing as needed assistance to the Biology, Dissolved Oxygen, and Board Chemistry Technical Leads with oversight of EPA, contractor, and grantee staff involved in all water quality survey activities associated with sampling, analysis, and data management activities in their functional areas
- Reviewing and approving technical work products related to the Water Quality Surveys
- Participating in meetings with the various team leaders, Technical Leads, the GLNPO QA Manager, and the GLNPO Director concerning Survey objectives, schedules, and concerns.

3.1.3.3 GLNPO Technical Leads

The Water Quality Surveys are supported by several Technical Leads who provide expertise and leadership in each of the survey's functional areas: board chemistry (Marvin Palmer), biology (Marc Tuchman), dissolved oxygen (Paul Bertram), and limnology (Glenn Warren).

Within GLNPO, the Technical Leads report to the persons indicated in Figure 3-1. For the Water Quality Surveys, they also report to the Environmental Monitoring Team Lead. Each Technical Lead is responsible for:

- Developing and implementing the aspects of this QAPP that relate to their functional area
- Daily oversight of EPA, contractor, and grantee staff involved in all onboard survey activities related to sample collection, analysis, and data management for their functional area
- Prior to each survey, randomly selecting site locations and depths for Rosette field duplicates (Board Chemistry Technical Lead only)
- Communicating survey objectives to all EPA, contractor, and grantee staff involved in the collection and analysis of survey samples (for their functional area)
- Reviewing and approving major deliverables related to Survey sample collection and analysis or data evaluation their functional area
- Participating in meetings with the Monitoring Team Leader, other Technical Leads, the GLNPO QA Manager, and the GLNPO Director concerning survey objectives, schedules, and concerns

- Approving methodologies, including method modifications, to be used for sampling and analysis of parameters in their functional area.
- Completing the Chief Scientist Roles and Responsibilities (listed in Appendix L) to verify that all project staff fulfilled the responsibilities described in this QAPP and that he has verified the accuracy of data collected and recorded during the cruise.

3.1.4 *Ship Operations and Safety*

Overall responsibility for safety operations within GLNPO lies with Louis Blume, the GLNPO Safety Officer. Safety management responsibilities within the Water Quality Surveys is delegated to George Ison, who also serves as the manager of Ship Operations during the Surveys. This approach ensures that decisions related to ship operations do not adversely affect ship safety procedures during the surveys (and vice versa). Specific responsibilities related of the Ship Operations and Safety Manager with respect to the Water Quality Surveys are described in Section 3.1.4.1. A second member of GLNPO's safety team is responsible for oversight of the contractor-provided Chemical Hygiene Officer (CHO). Because GLNPO does not have expertise in the area of chemical hygiene, this role is filled by a Safety Team member from Region 5. Section 3.1.4.2 describes the roles and responsibilities of the CHO Manager.

3.1.4.1 Ship Operations and Safety Manager

George Ison is a member of GLNPO's Safety Team, and reports directly to the Monitoring and Indicators Branch Chief. Under the Water Quality Surveys, Mr. Ison is responsible for:

- Oversight of the Ship Operations Contractor
- Scheduling all *R/V Lake Guardian* activities
- Developing and implementing procedures and training programs to ensure the safety of all operations staff and scientists participating in the surveys (and in other *R/V Lake Guardian* projects)
- Ensuring that all designated '1st responders' have received required training and/or re-certification as EMT's. (These 1st responders include the Chief Scientists, Shift Supervisor, First Mate, and Second Mate).
- Developing and implementing procedures to ensure that survey participants are sufficiently healthy to participate in survey activities and that appropriate medical precautions are taken when necessary
- Assisting the Team Leaders and Data Managers in considering ship operations and safety requirements when designing their survey objectives and plans
- Ensuring avenues of communication to and from the ship. This is primarily accomplished through electronic mail, cell phones, and facsimile. Responsible for making available an emergency phone number via satellite during cruises to allow for rapid communication in cases of emergencies.

3.1.4.2 Chemical Hygiene Officer (CHO) Manager

The Region 5 Safety Manager, Jim Finn, is responsible for oversight and management of survey activities performed by the CHO contractor. The CHO is provided by the Public Health Services. For the purposes of the Water Quality Surveys, the Region 5 Safety Manager reports to the Ship Safety Manager and to the GLNPO Safety Team Lead. Specific responsibilities include:

- Participation in the GLNPO Safety Team

- Ensuring that the CHO contractor has sufficient funds and tasking to deliver a qualified CHO for each survey
- Oversight and technical direction of the CHO
- Responding to technical questions and concerns raised by the CHO
- Acts as contact person to locate reagents onboard when survey staff need them.

3.1.5 Information Management Team

All data management activities are overseen by GLNPO's Information Management Team Lead, Pranas Pranckevicius, who reports directly to the director of GLNPO. He is responsible for ensuring that the resources, systems, and staff necessary to store, retrieve, and manipulate data gathered during GLNPO studies. He also is responsible for identifying and staying abreast of emerging technologies to ensure that GLNPO data management functions are up to date.

The Information Management Team Lead is supported by Ken Klewin, manager of the Great Lakes Environmental Database (GLENDA). GLNPO will begin capturing all survey data in GLENDA beginning with the 2000 surveys. As the manager of the GLENDA database, Dr. Klewin is responsible for:

- Ensuring the database is available to store survey data in a timely fashion
- Working with the Environmental Monitoring Team Lead, the Technical Leads, and the QA Manager to ensure that any modifications needed to ensure compatibility of GLENDA with survey requirements are implemented
- Developing and implementing systems for upload of survey data into GLENDA
- Developing and implementing appropriate database security and management procedures
- Implementing effective data retrieval procedures to facilitate use of data by GLNPO staff, contractors, grantees, and members of the scientific community
- Oversight of any contractor support required to modify the GLENDA database structure.

3.2 On-Ship Roles and Responsibilities

Due to the scientific and navigational nature of the surveys, dual lines of leadership and authority exist onboard ship. Ultimate responsibility and authority for all scientific and technical operations lies with GLNPO's Chief Scientist. However, the ship Captain has ultimate responsibility for all maritime and safety operations onboard ship, and the Captain has the authority to halt all scientific and technical operations when s/he considers it necessary to ensure the safety of all passengers and crew. In addition, contractors and grantees participating in the survey are responsible for reporting to their own management as well as to EPA scientists who provide them with site-specific instruction regarding sample collection, handling, and/or analysis. This instruction differs from technical direction in that it does not increase the level of effort or cost of existing tasking and focuses on the minor technical details (such as when to drop the winch) rather than significant instructions warranting formal contract management oversight.

All personnel that participate in GLNPO's WQS are required to complete and submit a Medical History Questionnaire for safety reasons. The Captain maintains these questionnaires in medical history envelopes for all survey participants in an onboard safe. This questionnaire is located in **Appendix G**.

GLNPO's Technical Leads (Figure 3-1) and other GLNPO staff serve as Chief Scientists onboard the vessel. A single Chief Scientists is assigned for each cruise staffing change by the Monitoring Team Lead through the Staffing Scheduling Form (Appendix C). Table 3-1 summarizes the roles and responsibilities of key technical staff involved in Water Quality Survey activities onboard the *R/V Lake Guardian*.

3.3 Contractor and Grantee Staff

All contractors and grantees supporting the Water Quality Surveys must have approved Quality Management Plans (QMPs) in place and operating prior to and throughout each survey. These approved QMPs shall clearly identify and define roles, responsibilities, authority, and lines of communication for all project staff involved in the management, implementation, QA, documentation, and survey activities. This includes, but is not limited to, a Project Manager responsible for oversight of all project activities performed by the contractor or grantee, a QA Coordinator or QA Officer that is independent of the project, a data management coordinator responsible for ensuring that all required hardcopy and electronic documentation is collected, stored, managed and reported in a manner that meets or exceeds the requirements of this QAPP, and all technical staff required to implement the scientific and technical activities (on ship and off ship) needed to fulfill the contractor's (or grantee's) requirements with respect to the Water Quality Surveys. In addition, all contractors and grantees collecting environmental data in support of GLNPO's water quality survey also have a QMP.

Table 3-1. Roles, Responsibilities, Authority, and Lines of Communication Onboard the R/V Lake Guardian During Water Quality Surveys

Organization	Role	Responsibility	Authority	Lines of Communication
EPA	Chief Scientist	<ul style="list-style-type: none"> All scientific and technical operations onboard ship during the surveys Ensuring all requirements of this QAPP are followed throughout the survey Ensuring that all EPA, contractor, and grantee staff adhere to applicable SOPs and collect and document all required data at all stations Ensuring adherence to all ship requirements (safety, etc) during surveys Ensuring the performance of and/or participating in technical systems audits Ensuring transport of samples to the contract laboratory Calls Science Meeting after ship sails 	<ul style="list-style-type: none"> Complete authority for all scientific and technical operations 	<ul style="list-style-type: none"> Communicates with Captain or senior officer on bridge Communicates with EPA, contractor, and grantee staff Reports to Monitoring Team Lead or WQI Branch Chief when in dock
	Shift Supervisor	<ul style="list-style-type: none"> Back up to the Chief Scientist (see above responsibilities) All scientific and technical operations when Chief Scientist is off duty 	<ul style="list-style-type: none"> Complete authority for all scientific and technical operations when Chief Scientist is off duty May be over-ruled by Chief Scientist 	<ul style="list-style-type: none"> Communicates with Captain or senior officer on bridge Communicates direction to all EPA, contractor, and grantee staff during his/her shift Reports to Chief Scientist while onboard ship
Ship Operations Contractor	Captain	<ul style="list-style-type: none"> Ultimate responsibility of ship safety Ensuring ship arrives at designated sites on schedule established prior to cruise Oversight of all ship contractor staff Ensuring all survey participants have practiced ship safety drill Collecting and documenting all bridge data as described in this QAPP and applicable SOPs Maintains medical history envelope for survey participants in an onboard safe 	<ul style="list-style-type: none"> Complete authority to halt scientific and technical operations when necessary to protect safety of crew and passengers 	<ul style="list-style-type: none"> Communicates direction to all ship operations contractor staff Communicates with Chief Scientist for site-specific instructions Contractually reports to Ship Operations Project Officer and Contracting Officer
	First Mate (or mate of the watch)	<ul style="list-style-type: none"> Back up to Captain when off duty (see above responsibilities) 	<ul style="list-style-type: none"> Same as above when Captain is off duty 	<ul style="list-style-type: none"> Reports to Captain Same as above when Captain is off duty
	Marine Technicians	<ul style="list-style-type: none"> Assist GLNPO scientists with sample collection activities Assist GLNPO scientist with "board chemistry" analyses in wet chem lab Understanding and implementing all QA/QC requirements in this QAPP 	<ul style="list-style-type: none"> None 	<ul style="list-style-type: none"> Supervised by Deck Officer Receive site-specific instruction from Chief Scientist/Shift Supervisor
	Able/Ordinary Seaman	<ul style="list-style-type: none"> Operate ship's mechanical sampling equipment, such as winches 	<ul style="list-style-type: none"> None 	<ul style="list-style-type: none"> Supervised by Deck Officer Receive site-specific instruction from Chief Scientist/Shift Supervisor

Organization	Role	Responsibility	Authority	Lines of Communication
Grantee	Biologist(s)	<ul style="list-style-type: none"> • All on board sampling, sample handling, labeling, and sample preservation activities related to zooplankton tows and benthos grabs in accordance with applicable SOPs • All on board sample handling, labeling, and preservation activities related to phytoplankton and chlorophyll a in accordance with applicable SOPs • Assistance with Rosette sampling when requested by GLNPO staff • Understanding and implementing all QA/QC requirements described in this QAPP • Informing Chief Scientist/Shift Supervisor of technical or QA issues • Informing technical staff of changes in required procedures 	<ul style="list-style-type: none"> • Senior biologist has authority over second shift biologist 	<ul style="list-style-type: none"> • Receives site-specific instruction from Chief Scientist/Shift Supervisor • Communicates through the Biology Technical Lead and Grants Officer
GLAS Contractor	Chemist(s)	<ul style="list-style-type: none"> • Assisting with Rosette sampling when requested by GLNPO staff • Adhering to all applicable SOPs to conduct all on board sample handling, preservation, and filtration activities related to nutrient and other chemical or physical analyses performed in a land-based lab by the GLAS contractor • Understanding and implementing all QA/QC requirements described in this QAPP. • Informing Chief Scientist/Shift Supervisor of technical or QA issues • Informing technical staff of changes in required procedures 	<ul style="list-style-type: none"> • Senior chemist has authority over second shift chemist 	<ul style="list-style-type: none"> • Receives site-specific instruction from Chief Scientist/Shift Supervisor • Communicates through the Limnology Technical Lead and Project Officer.
Public Health Service/ Region 5	Chemical Hygiene Officer	<ul style="list-style-type: none"> • Responsible for all aspects of chemical and chemical waste management • Calls Safety Meeting after ship sails • Manages onboard storage and control of chemicals • Disposes of laboratory chemical wastes • Verifies all onboard staff have turned in sealed medical questionnaires • Verifies all onboard staff have taken the laboratory safety course • Serves as back-up to Captain in ensuring all participants try on survival suits • Acts as contact person to locate reagents onboard when survey staff need them. 	<ul style="list-style-type: none"> • Require changes in chemical handling, management or disposal operations • Require changes in food management and handling operations 	<ul style="list-style-type: none"> • Reports to Jim Finn of Region 5 through Public Health Service • Takes survey-specific direction from Ship Operations Manager and Chief Scientist/Shift Supervisor

4.0 DATA QUALITY OBJECTIVES

4.1 Project Quality Objectives

As was noted in Section 1 of this QAPP, the Great Lakes Water Quality Surveys are intended to fulfill EPA's surveillance and monitoring obligations under Annex 11 of the Great Lakes Water Quality Agreement. In establishing this surveillance and monitoring program, the U.S. and Canadian governments stated their primary objectives in pursuing these activities were to evaluate the effectiveness of historical pollution control/pollution reduction strategies in the Great Lakes, identify emerging problems, and identify the need for new or revised strategies and further research. Given these objectives, GLNPO has designed the Water Quality Surveys to:

- Focus on key physical, chemical, and biological indicators of lake health
- Evaluate the health of each lake under different conditions (stratified and unstratified)
- Allow for real-time detection of significant changes in water quality, as indicated by significant changes in one or more parameters
- Provide data that can be compared from year to year
- Yield data that are of sufficient quality to support decisions regarding the need for further study or new pollution control strategies

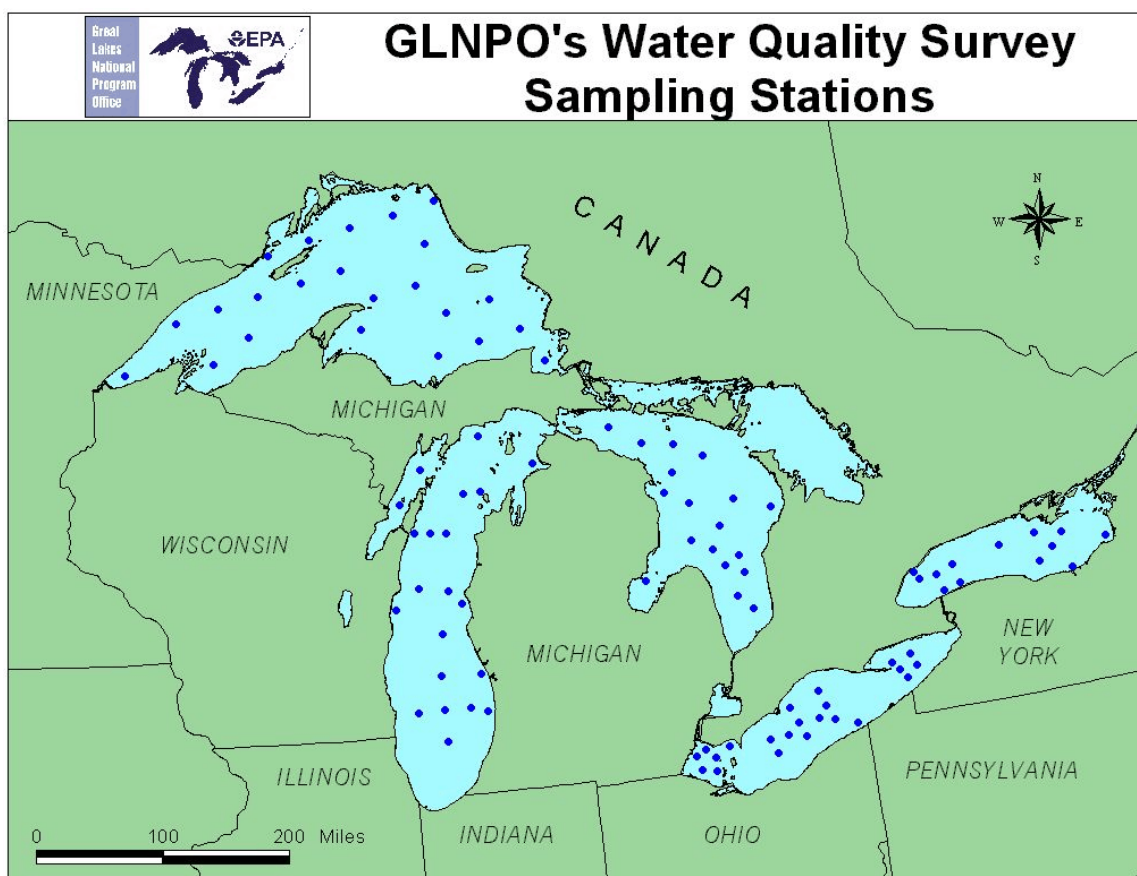
For the purpose of the surveys, GLNPO considers a significant change to be a 20% change from historical measurements made for a particular parameter in a particular lake during a particular season (e.g., a 22% increase of total phosphorus concentrations in Lake Huron over historical summer values). GLNPO also considers a reasonable potential for detecting such changes as an 80% likelihood that the change will be detected. Therefore, the data quality objective (DQO) for the Surveys is to "collect measurements that will yield an 80% chance of detecting a change of 20% or more within a particular lake and season, at the 90% confidence level". The key to meeting this objective is to minimize uncertainty. Major sources of uncertainty during the surveys include:

- (1) Sampling from a selected set of representative sampling stations instead of the entire lake
- (2) Variability in the sample collection process, and
- (3) Variability in the sample analysis process.

The issue of sample representativeness is addressed by the survey design, which is detailed in Section 7 of this QAPP. Briefly, the Survey design focuses on collecting samples from the same set of sampling stations each year. These stations are primarily located in 1) open lake waters (at least 13 kilometers from shore at least 30 meter depth) for water column sampling because historical data has shown that spatial variation in open water is small compared to variation nearshore and 2) shallower, nearshore waters for sediment sampling because historical data has shown that sediment changes in the open lake occur too slowly for detection on a year to year basis. Individual station locations for the survey were determined by EPA statisticians, working in conjunction with GLNPO scientists, who statistically evaluated historical data collected from intensive surveys of each lake to identify the optimum number of samples and sample locations needed to yield a representative sample of each lake basin. Figure 4-1 indicates the station locations selected in each lake.

Variability in the sample collection process will be controlled through the use of trained sampling teams, standardized, sample collection protocols, collection of field QC samples, and direct oversight of all activities by GLNPO's Chief Scientists. Details of these quality assurance techniques are given in Sections 5, 8, and 11 of this QAPP.

Figure 4-1. Sampling Stations for the Great Lakes Water Quality Monitoring Surveys



Similarly, variability in the sample analysis process will be controlled through the use of trained technicians and analysts, the use of detailed standard operating procedures (SOPs) for all field and laboratory activities, and the use of standard QC measures and pre-defined QC acceptance criteria with each set of analyses. Details of these QA techniques are given in Sections 5, 10, and 11 of this QAPP.

4.2 Measurement Quality Objectives

The physical, chemical, and biological parameters selected for inclusion in the study are listed in Table 2-1. All of the nutrient and biological parameters are considered to be key indicators of lake health. Most of the physical parameters are collected as supplementary data that are useful in interpreting the nutrient and biological survey results. As a result, measurement quality objectives (MQOs) for the physical parameters are not as stringent as those for the nutrient and biological measurements; the QC requirements described in this QAPP reflect this philosophy.

The following subsections and Section 11 of this QAPP provide details on how EPA's standard data quality indicators (precision, bias, accuracy, sensitivity, comparability, and completeness) will be monitored and controlled in this study. Representativeness is addressed above in Section 4.1.

4.2.1 Precision

Precision is the degree of agreement among replicate measurements of the same property, under prescribed similar conditions [2]. It can be expressed either as a range, a standard deviation, or as a percentage of the mean of the measurements (e.g., relative range or relative standard deviation). GLNPO

has established several approaches to measuring and evaluating precision during the surveys. The approaches vary according to monitoring parameter, expected variability, and importance of the measure to survey objectives.

Ideally, precision is measured by collecting two environmental samples at the same time (in the case of two sample collection devices) or sequentially (one device) and in the same place under the identical circumstances (same personnel, procedures, etc). Each sample is preserved and numbered separately and sent to laboratory as separate samples (coded FDn in the GLENDa database). Analysis of such duplicates allows data users to evaluate the precision of the entire data collection effort, including sampling, sample transport, and sample analysis. For the purposes of the Water Quality Surveys, the dual and sequential approaches are considered to be equivalent because historical experience indicates that minor time or spatial differences are not discernable in open lake measurements. In the Water Quality Surveys, field duplicates will be required for all total and dissolved grab parameters collected with the Rosette sampling device. These include:

- | | | |
|-------------------------------|-------------------------|------------------------|
| • $\text{NO}_2 + \text{NO}_3$ | • Reactive silica | • pH |
| • Total P | • Alkalinity | • Chlorophyll <i>a</i> |
| • TDP | • Turbidity | • Secchi Disk |
| • Chloride | • Specific Conductivity | |

In some cases, it is not feasible to collect true field duplicates or replicates; instead two or more subsamples can be split from the original sample by sampling personnel in the field. Each subsample is preserved and numbered separately, and the aliquots are sent to the laboratory as different samples. Although such splits do not contain the full component of measurement uncertainty (they contain uncertainty associated with field handling, laboratory preparation, and laboratory analysis procedures but do not include sample collection uncertainty), they are considered acceptable tools for measuring overall precision of those parameters in the Water Quality Surveys that are constrained by sample collection devices (such as limited bottles on the Rosette). These parameters include the particulate parameters which would require that a duplicate sample aliquot be processed through a separate field filter. Specifically, these parameters are:

- | | |
|-----------------|-----------------|
| • POC | • Particulate P |
| • Particulate N | • TSS |

Samples processed in this way during the Water Quality Surveys are identified as LDn in the GLENDa Database.

Note: Field duplicates are collected on grab samples only (no field duplicates or lab duplicates are collected on the integrated composite samples analyzed for phytoplankton and particulate nutrients).

Due to population variability among the zooplankton and benthic organisms, GLNPO will collect three zooplankton tows at each master station and three ponar grab samples at all stations for benthic organisms. Results for these three replicate field samples (i.e., numeric results such as biovolume) will be averaged and the standard deviation reported. Currently, no MQO has been established for the relative standard deviations among these field replicate measurements; GLNPO will establish one when sufficient historical data becomes available.

In other cases, the cost and value of collecting precision measures is not justified by the survey objectives. These cases include all physical measures that are collected to provide supplementary information that is useful in interpreting survey results but not critical to assessing lake health.

Measures of bias are collected for several of these parameters as shows in Table 11-4. Measures that fall in this category include:

- Aesthetics
- Optical transmittance
- Air and water temperature
- Wind speed and wind direction
- Water clarity
- Wave height
- Wave direction

For those parameters in which precision measures are required, GLNPO is compiling and evaluating historical data generated from the Great Lakes. GLNPO will use these data to generate statistically derived MQOs that reflect precision levels that realistically can be achieved with the sampling and analysis methods specified in this QAPP. In the meantime, GLNPO's interim MQO for survey precision is that chemistry and physical results from 90% of these duplicate or split pairs agree within +/- 50% for values greater than 5x the method detection limit and that 90% of these duplicate or split pairs agree within +/- 100% for values less than 5x the method detection limit. No interim MQOs have been established for the biological parameters.

In addition to the use of field duplicates and field splits to assess *overall* measurement precision, laboratory staff will employ several types of laboratory QC measures (e.g., laboratory reference samples, laboratory performance check samples, laboratory duplicates, etc.) that provide information about the precision associated with various components of the analysis process. These QC elements and associated requirements are described in greater detail in Section 11 (Quality Control Requirements) of this QAPP. It should be noted that survey DQOs are based on overall data quality, and failure to meet any single laboratory precision measure does not automatically imply the data are unacceptable for use in this study. Instead, laboratory QC measures are used to monitor and control precision in real time so that overall precision goals are met. Details regarding the data quality assessment process governing use of survey data are given in Sections 16, 17, and 19.

4.2.2 Bias

Bias is the systematic distortion of a measurement process that causes errors in one direction [2]. Bias in the Water Quality Surveys is measured through analysis of analytical standards of known concentration, comparison among multiple instruments, and the participation in intercomparison studies when resources allow. Control of bias also is assured through regular factory calibration of instrumentation. Bias objectives and goals are currently limited to analytical chemistry measurements because 1) no source of standard reference materials or intercomparison study samples exists to allow for determination of biological measurement bias, 2) the cost of collecting bias measures on the physical measurements is not justified by survey objectives. When intercomparison studies are conducted, GLNPO's MQO for bias is that GLNPO results fall within two standard deviations of the mean study results.

At a less formal level, GLNPO's Technical Leads routinely make scientific assessments of data quality as part of their routine data evaluation and analysis activities. Because lake chemistry changes slowly and the Technical Leads are experts in recognizing measurement anomalies within each lake, their interpretation of potential measurement bias can be quite valuable and will be used as a QA tool within the Water Quality Surveys.

In addition to the use of intercomparison studies and best professional judgement to assess *overall* measurement bias, laboratory staff will employ several types of laboratory QC measures (e.g., instrument calibration standards, method blanks, etc.) that provide information about the bias associated with various components of the analysis process. These QC elements and associated requirements are described in greater detail in Section 11 (Quality Control Requirements) of this QAPP. It should be noted that survey DQOs are based on overall data quality, and failure to meet any single laboratory bias measure does not

automatically imply the data are unacceptable for use in this study. Instead, laboratory QC measures are used to monitor and control bias in real time so that overall bias goals are met. Details regarding the data quality assessment process governing use of Survey data are given in Sections 16, 17, and 19.

4.2.3 Accuracy

Accuracy is a measure of the closeness of an individual measurement or the average of a number measurements to the true value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that result from sampling and analysis operations. Accuracy is best determined by routinely analyzing a reference material of known concentrations or by reanalyzing a sample spiked with a known amount of pollutant [2]. Because accuracy is a function of precision and bias, GLNPO will control survey accuracy through the precision and bias strategies described in sections 4.2.1 and 4.2.2.

4.2.4 Sensitivity

Measurement sensitivity is defined as the minimum concentration of an analyte above which a data user can be reasonably confident that the analyte was reliably detected and quantified. Above the detection limit is the level at which reliable quantitative measurements can be made. This level is generically termed the "quantification limit" or "quantification level" and it usually represents a multiplier (typically between 3 and 5) of added certainty above the detection level.

Measurement sensitivity includes many components of variability, including variability of the measurement device (instrument), variability of the sample preparation process, and variability introduced during sampling. As a result, a myriad of detection limit concepts exist, including instrument detection limits (IDLs), method detection limits (MDLs), and system detection limits or SDLs. Although the details and emphasis of the various sensitivity concepts vary, nearly all definitions of detection limits are based on statistical analyses of laboratory data. To determine an MDL using EPA's 40 CFR part 136 B approach, for example, at least seven replicate samples with a concentration of the pollutant of interest near the estimated MDL are analyzed. The standard deviation among the analyses is determined and multiplied by 3.14. The result of this calculation becomes the MDL. The factor of 3.14 is based on a t-test with six degrees of freedom and provides a 99 percent confidence that the analyte can be detected at this concentration. Similarly, a common method for determining the IDL is to inject several blank replicates or low concentration standard replicates into an instrument and calculate a limit based on the standard deviation of the responses. System detection limits are often determined by determining the standard deviation of replicate field blank measurements.

Because the data collected in the Water Quality Surveys will be used to support decisions regarding areas of further study and will not be used for regulatory compliance or enforcement purposes, GLNPO's objectives for determining and monitoring measurement sensitivity are based on: 1) the need to use methods capable of detecting changes in water quality and 2) using the most pragmatic approach to collecting this information. To ensure that methods used in the study are capable of detecting change, the methods must be sensitive enough to detect the target parameters at the concentrations currently found in the lakes. Where feasible, method sensitivity should be at least 3-5 times lower than the concentrations historically found in the lakes so that results reported in the surveys can be considered to be both quantitatively and qualitatively accurate. For parameters that are likely to be influenced by background contamination, method sensitivity should be at least 10x lower than historical lake concentrations so that actual results reported can be reliably distinguished from any effects of contamination. Table 4-1 lists sensitivity goals for each chemistry parameter. These goals reflect historical data collected in the lakes.

Presently, only one parameter (total dissolved phosphorous) is barely meeting the sensitivity objectives listed in Table 4-1. Although solutions, such as the use of alternate analysis methods, do exist, the costs of such solutions may outweigh the benefits. Therefore, GLNPO is currently evaluating these costs and benefits and will determine if changes to the measurement procedures are needed prior to future surveys.

For each chemical method, Method detection limit (MDL) studies should be performed according to 40 CFR, part 136, Appendix B (if applicable), or by another procedure that is pre-approved by the WQS QM Technical Lead or the GLNPO QM. MDL studies must be conducted once per year and each time a significant change is made to the analytical SOP, including changes in instrumentation.

As noted above, GLNPO's objective for measuring sensitivity is to use the most pragmatic means available given study objectives and already known contributions to measurement uncertainty. Ideally, for example, sensitivity is defined through the use of a system detection limit concept, because this concept takes into account the sensitivity of the entire measurement process (field, laboratory, and instrument). In practice, however, it is difficult and costly to collect and analyze replicate field blank samples. In addition, the effects of field procedures on measurement sensitivity are usually small compared to the effects of analysis method and instrument variability. The exception to this rule is for ubiquitous pollutants, such as metals, that can contaminate samples at extremely low concentrations in the field. None of the parameters monitored in the surveys fall into this category; therefore, determination of system detection limits is not necessary for the survey, although they are determined for some analytes.

Similarly, the meteorological data collected from the Danforth Marine Indicator are ancillary to the primary survey objectives. Therefore, a formal determination and verification of instrument or method sensitivity by Survey staff is not necessary; instead, GLNPO relies on the biannual calibration and certification of the instrument by its manufacturer.

Table 4-1
Sensitivity Objectives for Water Quality Survey Parameters

Parameter	Sensitivity Objective
NO ₂ /NO ₃	0.03 mg N/L
Particulate Nitrogen	.03 mg N/L
Particulate Organic Carbon	5.0 µg C/L
Dissolved Organic Carbon	not specified
Total Phosphorus	1 µg/L
Total Dissolved Phosphorus	1 µg/L
Particulate Phosphorus	1 µg/L
Chloride	0.03 mg Cl/L
Reactive Silica	0.010 mg Si/L
Specific Conductance	not specified
Alkalinity	not specified
pH	not applicable
Total Suspended Solids	not specified
Dissolved Oxygen	0.1 mg/L

4.2.5 Representativeness

Representativeness is a measure of the degree to which data accurately and precisely represent a characteristic of a population parameter at a sampling point or for an environmental condition. It is a qualitative term that is evaluated to determine if data appropriately reflect the media and phenomenon being measured or studied. [2] As indicated in Section 4.1, the sampling stations selected for the Water Quality Surveys were chosen so that the target populations are represented by valid sub-samples. As resources allow, GLNPO will periodically assess results of its survey activities over time to verify that the statistical power originally anticipated for the study is still being met.

4.2.6 Completeness

Ideally, GLNPO and contractor/grantee scientists will be able to collect a complete suite of data from all stations in all surveys. In practice, however, a lower level of completeness can still lead to a valid study. If a significant lack of completeness is obtained in a particular survey (cruise), causes of the problem(s) will be investigated and lessons learned will be incorporated into planning of future surveys. When samples are not collected at a station, the reason will be documented by the Chief Scientist. The remarks column on the data forms (located in Appendix H) can be used for this purpose.

4.2.7 Comparability

Comparability expresses the confidence that two data sets can contribute to a common analysis and interpolation. Because the surveys involve the collection and analysis of numerous samples during different seasons and years, data will be generated from samples collected by different sampling teams and analyzed by multiple laboratory staff and organizations. To ensure comparability among these data sets, GLNPO and its team of contractors and grantees will:

- Employ standard operating procedures for sample collection (or require that their contractors and grantees employ such SOPs)
- Employ or require use of detailed analytical methods/SOPs specifying each step of the laboratory process

- Use one method/SOP for all analyses of a given pollutant, unless significant improvements to measurement techniques are identified. In such cases, the Technical Lead and QAM will evaluate the potential impacts of method changes before approving their use.
- Offer an annual training session on the SOPs used onboard the vessel
- Ensure that the Chief Scientist oversees all onboard sampling and analytical activities
- Specify method detection limits and QC acceptance criteria that must be met throughout the surveys
- Specify data reporting formats and units that must be used by all survey participants
- Use a standardized data quality assessment process

5.0 SPECIAL TRAINING REQUIREMENTS

All EPA, contractor, and grantee staff participating in the surveys must be fully trained in onboard safety requirements and any scientific functions for which they are responsible. Survey scientists involved in sample or data collection also must be trained to use the equipment and procedures specified in this QAPP. In addition to training received prior to boarding the ship, all new staff responsible for performing scientific activities onboard ship are provided with hands on training and supervision by senior scientists during the first few days of each survey. Further, the Chief Scientist conducts a science meeting at the start of a survey and with each new crew change. Logistics, roles and responsibilities, and special objectives of the survey are presented and any questions addressed.

Training responsibilities vary according to specialty. GLNPO is responsible for providing all safety training and for training survey scientists in the use of the Rosette sampling device, the collection of onboard measurements using the SeaBird, and the use of specific instruments and techniques for measurement of other physical parameters. The biology grantee is responsible for training its staff in the collection and analysis of biological parameters of interest. Similarly, the GLAS contractor is responsible for training its staff in the collection and analysis of nutrient parameters of interest. In addition, the GLAS contract and the grant agreement specify minimum skills (i.e., education and experience) required of the analysts performing work under these vehicles.

Specific training requirements will include some or all of the following courses, depending on the specific responsibilities of the survey participant(s).

- 24-hour Laboratory Safety Course/4-hour Laboratory Safety Refresher Course (required for all government, contractor, and grantee survey scientists working in the ship laboratory)
- First Aid, CPR, EMT training for all designated 'first responders' (Chief Scientist, Shift Supervisor, First Mate, and Second Mate)
- Fire Fighting (required for the contractor-provided ship operating personnel)
- Powered Industrial Trucks/fork lifts (required for the contractor provided ship operating personnel)
- GLNPO Chemical Hygiene Plan
- Safety Orientation Video (required for every individual that participants in cruises, regardless of responsibility)
- Boat Handling and Seamanship (required of the contractor-provided ship operating personnel)

Additional information concerning safety training procedures and requirements can be found in GLNPO's *Health, Safety, and Environmental Compliance Manual* (May 1997 or as amended).

All staff involved in the Water Quality Surveys are responsible for ensuring that they have received the required training and that their training is up-to-date. Each individual participating in the survey also is responsible for completing and submitting to the QA Manager a Self-Certification form (Appendix F of the WQS manual) that certifies s/he has completed all required training. The QA Manager is responsible

for ensuring that all survey participants have completed and submitted this form prior to the start of the cruise.

6.0 DOCUMENTATION AND RECORDS

Formal chain of custody procedures are not required for the Water Quality Surveys because survey data are not used for enforcement or compliance monitoring activities. Instead, GLNPO employs several QA strategies to ensure that samples are accurately documented and tracked throughout the sample collection, handling, transport, analysis, and reporting processes. These include the use of centralized sample identification numbers that are pre-assigned by GLNPO before each survey and strict Record keeping requirements employed by all staff throughout the surveys. These requirements are described in Sections 6.1 and 6.2 respectively.

In addition, a series of forms are used to document specific processes employed during implementation of the surveys. **Appendix C** contains a staff scheduling form that lists shift dates for proposed and actual GLNPO staff participating in the survey. **Appendix E** contains survey planning forms that must be submitted by researchers requesting use of the Lake Guardian for sampling purposes. **Appendix F** contains the self-certification form that all GLNPO staff and contractors/grantees participating in the survey must complete and provide to the GLNPO QA Manager to certify their meeting pre-survey training requirements as specified on the form. **Appendix G** contains the Medical History Questionnaire that is required to be completed and submitted by all personnel that participate in GLNPO's WQS. **Appendix L** contains a list of roles and responsibilities for the Chief Scientist, in addition to a list of priorities for each staffing period and a checklist that must be completed by the shift supervisor for each shift of 12 hours and provided to the QA Manager to verify that they met their responsibilities involving ship operations and survey data management. **Appendix M** contains a suggested revision sheet that survey participants should use to document issues, errors, and suggested revisions and clarifications to the manual. **Appendix N** contains a data status tracking sheet to track specific data sets throughout the data verification process and upload to the GLENDa database. **Appendix O** contains a data discrepancy form to initiate a revision to the GLENDa database when errors are identified. Finally, **Appendix Q** contains the station location change form that must be completed and approved by pertinent survey participants to finalize a change to a station location.

6.1 Sample Identification and Labeling

Sample definition and numbering: Prior to each survey, the Technical Lead for Board Chemistry will create and assign unique sample numbers for each sample to be collected during the survey. This approach ensures that there is no confusion among scientists and staff during data gathering, data reporting, or data evaluation concerning sample identity. For the purposes of the Water Quality Surveys, a sample is defined as a discrete volume of water or sediment collected with a particular type of device at a particular site and depth on a given day. A sample may then be aliquotted into several fractions and bottles for analysis of different parameters. Each of these bottles is given the same sample number. Field duplicates and blanks are treated as separate samples and, therefore, assigned different sample numbers.

Pre-labeled bottles and containers: Prior to each survey, the Board Chemistry Technical Lead creates computer-generated sample labels that are pre-affixed to each cubitainer and bottle that will be used to store samples in the field. Copies of these labels also will be affixed to the cubitainer or bottle cap to serve as a back up means of identification should the labels come off during sample processing. To further ensure that samples are properly identified and handled in the field, each sample label will be color coded to indicate the preservation and filtration requirements needed for each sample bottle (i.e., yellow labels are used for total nutrient aliquots requiring preservation with sulfuric acid, orange labels

are used for total dissolved nutrients which are filtered and preserved with sulfuric acid, and white labels are used for unpreserved sample aliquots).

Prior to arrival at a sampling station, the labels for the associated samples will be segregated and applied to the sampling bottles. When sample bottling and preservation are completed, a record of the numbers on the labels used will be made on analysis request sheets. The analysis request sheet will be used to track samples through the processing and analysis.

Label information: Each sample label will contain the following information:

- A 9-digit sample number (coded as described below) that is unique to the sampling date, location, depth and sampling device
- Lake
- Station number
- Survey data
- Preservation used
- Parameter to be measured

Sample numbering scheme: Each sample number is coded in the following format to provide summary level information about the sample:

<u>Year</u>	<u>Sample Device</u>	<u>Lake</u>	<u>Series</u>	<u>Sample Type</u>	<u>Sample Number</u>
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Valid codes for the sample numbers are as follows.

<i>Year:</i>	two digit years such as “00”, “01”, “02”
<i>Division:</i>	G for GLNPO
<i>Lake:</i>	A = Michigan; B = Huron; C = Erie; D = Connecting Channels; E = Ontario; S = Superior
<i>Series:</i>	Number sequence
<i>Sample Type:</i>	S = Primary; I = Integrated; D = Duplicate; R = Field Blank; C = Duplicated Analysis; X = Spike; and B = Laboratory Blank.

In addition, samples that are collected for production of the integrated sample only (i.e., they are not otherwise collected for determination of study parameters but solely for production of the integrated sample), will be identified with an a, b, or c at the end of the sample number.

Station Identification: To avoid confusion regarding station identification between lakes (i.e., to distinguish between Lake Erie Station 61 and Lake Huron Station 61), GLNPO assigns a “Station ID Number” to each station visited. The Station ID number consists of the first two letters of the lake name followed by a space and the 2-digit station number (a leading zero is added to single digit station IDs). For example, Lake Erie Station 61 is assigned the Station ID “ER 61” and Lake Huron Station 61 is “HU 61”. Historically, a different numbering system was used for Lake Superior, but to improve consistency, sampling stations for Lake Superior are now numbered SU 01 - SU 19.

Visit Identification Numbers: GLNPO also assigns unique “Visit ID” numbers to differentiate sampling activities conducted at a single site on different dates (or visits). The Visit ID number consists of the first letter of the lake name followed by the 3-digit station ID (leading zeros are added for one or two digit station IDs) followed by the first letter of the month the survey began and the last two digits of the survey

year. In order to give each month a unique identifier, Y is for May, U is for June, L is for July and G is for August. For example, if Lake Erie Station 61 is visited in the spring of 2000, and the spring surveys begin in April, the Visit ID assigned to this station on the spring cruise is "E061A00".

Time definitions: While surveys are in progress, a single 'ship time' is used throughout the survey regardless of the time zones crossed during transit. Therefore, all survey participants are required to synchronize their watches with 'ship time' when they board ship. Because the world standard for time keeping is Greenwich Mean Time (GMT), all electronic measurements made on the bridge are captured in GMT. To facilitate conversion between GMT and ship time, the "mate of the watch" also records the 'correction factor' (e.g., 5 hours) for converting GMT to the time zone standard (e.g., eastern daylight time, central standard time, etc.) used at the ship location. The correction factor is entered into GLENDa along with the actual time measurements recorded by scientists and bridge staff when the data are uploaded to the database. Once in GLENDa, data users can specify the time standard they need when retrieving data.

6.2 Record keeping

The Chief Scientist has primary responsibility for assuring that all data gathered in the survey is documented through a combination of manual and electronic procedures as described below. Documentation includes raw instrument level printouts, summary bench sheets, hard-copy field information recording forms, and electronic records generated on board ship and in the laboratories.

All shipboard-generated strip charts, bench records, and computer printouts are kept in a folder, indexed by station, until the remaining samples are transferred to the land-based laboratory. All raw data are assembled and indexed by parameter, by lake, and by survey leg. Analog charts and digital conversion printouts will be stapled together. Each parameter will be placed in manilla folder and transferred to the GLNPO Chief Scientist for Board Chemistry upon conclusion of the survey. Several parameters are recorded on the ship's log, such as vessel position and weather conditions. This information is described in LG 300, *SOP for Meteorological Data Aboard the R/V Lake Guardian*. These parameters are then recorded on the GLENDa Station Information Field Recording Form at each station visit and entered into the GLENDa database.

Hard-copy Field Information Recording Forms (located in Appendix H of the WQS manual) are used to record data as it is being collected during the survey. GLNPO has developed 16 hard-copy data forms for capturing all required data for the survey as well as supplementary data, such as weather. These 16 forms are:

- 1) Survey Information
- 2) Station Information
- 3) Rosette Sampling Data
- 4) Ponar Grab Sampling Data
- 5) Zooplankton Net Flowmeter Calibration
- 6) Zooplankton Sampling and Secchi Disk Data
- 7) Chlorophyll *a* Preparation
- 8) Phytoplankton Preservation
- 9) Nutrients Preparation
- 10) POC, PN, PP Preparation
- 11) TSS Preparation
- 12) Preparation of Quality Assurance Samples
- 13) Calibration Data of Board Chemistry Instruments plus Shiftwise Standardization
- 14) Control Standards Data of Board Chemistry Parameters
- 15) Board Chemistry Data

16) Dissolved Oxygen Data (Winkler)

The data reporting forms listed above are intended to capture information about discrete measurements. In addition, GLNPO collects extensive electronic data that is gathered continuously on the bridge at all times while at sea and continuously by the SeaBird when the probe has been dropped. Bridge data concerning temperature, barometric pressure, ship heading, depth, apparent wind angle and speed, GPS position, Greenwich Mean Time, Greenwich Mean Day, course over ground, waypoint position (station location), and bearing and range to waypoint are averaged every 15 minutes and stored on disk. One disk per lake per survey is used to store all such electronic data from the bridge. SeaBird measurements are averaged every half meter and stored using the SEASAVE software program which facilitate conversion of the data to graphic or tabular format.

During the surveys, data are entered into an onboard data entry system, the GLENDa remote data entry tool, designed to capture survey data into the database on a daily basis. A User guide for the tool is located in Appendix J of the WQS manual. This system, available on the *R/V Lake Guardian* and at GLNPO headquarters, is designed to include real-time data entry checks to prevent analysts or technical staff from entering 'nonsensical' values. The tool is based on a windows interface to the GLENDa database and is intended to allow the easy input of field data from prescribed field information recording forms mentioned above. The items from the recording forms are copied to corresponding locations on the windows input sheets. If the tool is not functioning properly, the data can be entered into Excel electronic files, which are a soft-copy version of the recording forms in Appendix H of the manual, as a back-up to the tool. If this back-up option is used, the data are entered into the Remote Data Entry Tool from these electronic files at GLNPO headquarters or onboard the ship if the Remote Data Entry Tool begins to function during the survey leg. Once the data are in the Remote Data Entry Tool they are uploaded to GLENDa as unverified data. A Data Flow Diagram is provided in Figure 1, of SOP LG101 of the WQS manual, and presents the data management process for data collection and data verification for the WQS.

The Chief Scientist is responsible for transferring the original field information recording forms to the QA Team at GLNPO (Marvin Palmer or his designee) for internal quality control checks. The QA Team conducts checks of the recording forms against the data that has been uploaded to GLENDa and addresses any data discrepancies. After completing these checks and resolving all discrepancies, the QA Team transfers the forms to the Environmental Monitoring and Indicators Team for storage in the designated file cabinet at GLNPO. The pertinent Technical Lead conducts a final review of the data and notifies the Database Manager of approval. The Database Manager then finalizes the dataset as Version 1 and makes the data available. For each dataset, the status of this data management process is tracked by the QA Team on the Data Status Tracking Sheet (Appendix N of the WQS manual).

The Chief Scientist must assure that a copy of the hard-copy field information recording forms is made and placed in the onboard designated file cabinet at the end of each survey leg. The Chief Scientist assures that an electronic copy of all soft-copy field information recording forms is made and transferred to the database manager at GLNPO (Ken Klewin) for storage. The Chief Scientist also must assure that SeaBird data files are processed at the end of each survey leg and returned to the database manager for storage. These items are included on the list of Chief Scientist Roles and Responsibilities (Appendix L of the manual). For the bridge data, The Officer in Charge shall be responsible for reviewing the previous watch entries in the Ships's Log, GLENDa Station Information Field Recording Form and the GLENDa database to assure correctness of the data entered. Errors noted shall be corrected immediately.

A process also has been developed for correcting errors identified in verified data in GLENDa and is illustrated in Figure 2 of SOP LG101 in the WQS manual. Once a data error is identified, a Data Discrepancy Form (Appendix O of the WQS manual) is completed and submitted to the Quality Assurance Manager and Database Manager. Data are revised in GLENDa and the revisions are verified as correct by the QA Team. The pertinent Technical Lead also conducts a final review and notifies the

Database Manager of approval. The Database Manager then finalizes the dataset as the subsequent version and makes the data available.

Results generated in land-based laboratories will be reported on laboratory-specific data forms (i.e., the laboratories are allowed to design and submit their own data reporting format that complies with GLNPO's data entry standard and is subject to GLNPO approval).

Additional information concerning Record keeping procedures can be found in the Water Quality Survey SOP LG101, *Electronic Field Information Recording*.

7.0 SAMPLING PROCESS DESIGN

The sampling design reflects the need to collect data from sites, depths, and times that are representative of lake conditions. Section 7.1 summarizes the design strategy for selecting representative stations, Section 7.2 summarizes the design strategy for selecting representative sampling depths at each station, and Section 7.3 summarizes the strategy for selecting representative sampling frequencies at each station and depth.

7.1 Site Selection Strategy

All sampling stations selected in the survey were chosen by scientists and statisticians using 1) historical data from intensive lake studies (which indicates that spatial variation in open lake waters (more than 13 kilometers from shore and greater than 30 meter depths) is small compared to nearshore spatial variation, and 2) the Water Quality Survey objective of detecting a 20% change from year to year.

Using this approach, stations for water column sampling were selected from homogenous areas of each lake where routine variability in lake conditions would not likely mask actual changes. In contrast, locations of benthos stations were selected to provide coverage of both the offshore benthic communities at a variety of depths, and selected nearshore sites of specific interest. [3, 4, 5, 6] Over time, actual station locations have been modified to reflect new data, information, and priorities. The water column and benthic monitoring stations currently used during the surveys are shown in Appendix A of the Water Quality Survey procedures manual, titled, *Sampling and Analytical Procedures for GLNPO's Open Lake Water Quality Survey of the Great Lakes*, March 2003 (or as amended). These stations also are described in Attachment A of this document, Tables A-1 through A-18.

In addition to the routine monitoring stations, "master stations" have been identified in each major lake basin. The routine monitoring stations are referred to as non-master stations. Originally, two master stations were selected for each basin, with one master station being sampled on the way out and the other being sampled on the return trip. The intent was to provide a form of replication to ensure that the data collected during each survey would not be biased by transient effects. Most of the current master stations represent the deepest point within its lake basin. These stations are sampled at more frequent depths to provide GLNPO with a better means of characterizing vertical conditions during each survey. Master stations identified for each lake basin are shown in Table 7-1.

In the event that a station location needs to be changed (e.g., when the biology team searches for a depositional zone and would like to designate the coordinates of the new station location) certain steps should be followed to assure that the proposed change is approved, all participants are notified, and that all documentation are updated. Further, these steps will ensure that all documents, publications, and databases use the same finalized (current) station coordinates. The master list of station location coordinates will be posted on GLNPO's website, as well as in GLNPO's shared "Base Monitoring Program" directory.

To change a station location, the form GLNPO's Base Monitoring Program Station Location Change Form, located in Appendix Q, needs to be completed by filling in the following fields: station ID, old coordinates, new coordinates, new depth, the reason for the station location change, and the person's name who is requesting the change. The completed form should be submitted to the appropriate technical lead (Glenn Warren for open water stations and Marc Tuchman for benthos stations). Once the technical lead approves the change, he needs to sign and date the form.

The completed form needs to be initialed by GLNPO's Monitoring Team Leader to give final approval to the station location change, and then initialed by the Captain verifying that the ship's GPS unit has been updated. The form must then go to the GLENDa database manager who will initial it, file it, and update the master station location list. Before a new version of the SOP manual is released, these changes must be incorporated into the WQS QAPP and the Lake maps updated.

For consistency, new station location coordinates should be rounded to the nearest whole second of arc, decimal degrees should be limited to five significant digits, and decimal minutes should be limited to three significant digits.

Table 7-1. Master Station Locations for the Water Quality Surveys

Lake	Basin	Master Stations
Michigan	southern lake	Station 18
	central lake	Station 27
	northern lake	Station 41
Huron	northern lake	Stations 45 and 54*
	central lake	Not applicable
	southern lake	Station 15
Erie	western lake	Station 91
	central lake	Station 78
	eastern lake	Station 15
Ontario	western lake	Station 33
	eastern lake	Station 55
Superior	western lake	Station 17
	central lake	Station 08
	eastern lake	Station 01

* Two master stations in northern Lake Huron are an artifact of the historical two station approach

7.2 Depth Selection Criteria

Sampling depths vary according to the condition of the lakes (stratified versus unstratified conditions) and the parameter of interest (for example, benthic organisms are only found on the lake bottom while phytoplankton congregate at the upper depths of the lake). Further, these strategies vary depending if samples are being collected from a master or non-master station.

In general, the *spring survey strategy* is to collect samples from the surface, mid-depth, near bottom and bottom depths of each lake to gather information about the lake during unstratified, or isothermal, conditions. In general, the *summer survey strategy* is to collect samples from the surface, mid-epilimnion, lower epilimnion (master stations only), mid-hypolimnion (non-master stations only and Lake Erie central basin master station), thermocline (master stations only), upper hypolimnion (master stations only), deep chlorophyll layer (if present), near bottom, and bottom depths of each lake to gather information necessary to characterize the lake during stratified conditions. During spring and summer surveys for master stations, samples also are collected at discrete depths throughout the water column. In addition, integrated composite samples are collected for determination of several parameters of interest. These depths, and the parameters sampled at each depth are detailed in Table 7-2.

Table 7-2. Sampling depths and parameters measured in each season

Depth Description	Season(s) Sampled	Parameters Monitored
Surface (SRF, 1 meter below surface)	spring and summer	Nitrate + Nitrite, Total Phosphorus, Total Dissolved Phosphorus, Chloride, Reactive Silica, Turbidity, Specific Conductance, pH, Dissolved Oxygen, and Chlorophyll a
Mid-depth (varies according to site)	spring (non-master stations only)	
Mid-epilimnion (MEP, depths vary)	summer	
Lower epilimnion (LEP, depths vary)	summer (master stations only, excluding Lake Erie Central and Western basins)	
Thermocline (TRM, depths vary)	summer (master stations only, excluding Lake Erie Central and Western basins)	
Upper hypolimnion (UHY, depths vary)	summer (master stations only, excluding Lake Erie Central and Western basins)	
Mid-hypolimnion (MHY, depths vary)	summer (non-master stations only and Lake Erie Central basin master station)	
Discrete depths including 5 m, 10 m, 20 m, 30 m, 40 m, 50 m, 100 m and 200 m (as station depth allows)	spring (master stations only) and summer (master stations only, excluding 5 m, 10 m, 20 m and 30 m)	
10 meters from the bottom (B-10)	spring (excluding Lake Erie Central and Western basins) and summer (for Lake Erie, only Eastern basin master station)	
2 meters from the bottom (B-2) in all lakes excluding Lake Erie	spring (at all master and non-master stations only if inverse stratification is present) and summer (at all master and non-master stations only if nepheloid layer is present)	
1 meter from the bottom (B-1) only in Lake Erie	spring and summer	Phytoplankton, Chlorophyll a, Total Suspended Solids, Particulate Organic Carbon, Particulate Total Nitrogen, Particulate Total Phosphorus, Chloride, Silica, Total Phosphorus, Total Dissolved Phosphorus, and Nitrate + Nitrite
Deep Chlorophyll Layer, if present (DCL, depths vary)	summer	
Integrated sample of the upper lake (SRF = 1 m, 5 m, 10 m, and 20 meters) ^a	spring	
Integrated sample of the upper epilimnion (SRF = 1 m, 5 m, 10 m and LEP) ^b	summer	Benthos in spring Benthos, Grain Size, Total Phosphorus ^c , Total Organic Carbon ^c and Total Nitrogen ^c in summer
Bottom sediments	spring and summer	
From 20 meter depth to surface	spring and summer	
From B-2 to surface or from 100 m to surface whichever is less	spring and summer	Zooplankton

^a For an unstratified water column, the integrated sample is prepared by taking equal volumes of water from SRF (1 m), 5 m, 10 m and 20 meters unless the depth is less than 20 meters. If the total depth is between 15 and 22 meters,

the 20 meter sample is replaced by the bottom sample (B-1 or B-2). If the total depth is less than 15 meters, equal volumes are taken from surface, mid-depth, and bottom sample (B-1 or B-2).

^b For a stratified water column, equal volumes are taken from the surface, 5 m, 10 m, and lower epilimnion (LEP). If the epilimnion is very shallow, equal volumes are taken from a maximum of four sampling depths and a minimum of two sampling depths. The underlying strategy is to collect a representative sample from the epilimnion. See in Appendix P, Integrated Sample for a Stratified Water Column.

^c These parameters are not determined every year.

NOTE: A suite of physical parameters, such as specific conductance and temperature, also are monitored with the SeaBird CTD (see section 8.1 and LG302, *Operating the SeaBird CTD*).

7.3 Sampling Sequence/Frequency Strategy

Sampling events during the cruises follow the general outline described below, with minor variations made on-site as necessary to accommodate weather, sea, and other conditions.

Sample Type	Sampling Strategy
Visual and Physical Observations	<ul style="list-style-type: none"> Record wind speed and direction, wave height and direction, air temperature, barometric pressure, visibility, weather conditions, and heading (when underway) each hour on the hour Record station identification, arrival time, departure time, wind speed and direction, wave height and direction, barometric pressure, water depth, air temperature, geographic location upon arrival, and final location (if vessel drifted during sampling) at each sampling station. Record deviation of ship time from Greenwich mean time daily.
Rosette samples	<ul style="list-style-type: none"> Run Rosette/CTD down to define the temperature profile and determine the thermal structure. The Chief Scientist or Shift Supervisor will examine the CTD profile. The Chief Scientist or Shift Supervisor and the Marine Technician will select sampling depths according to depth selection strategy for each lake (See LG200, Section 4.0, Sample Depth Selection, for detailed information on selecting station depths and Appendix B, Attachment A for a detailed list of monitoring stations and depths). During unstratified conditions that occur in the Spring, most of the sample depths are constant, however, the CTD profile is used to determine whether inverse stratification is present and sample accordingly. During stratified conditions that occur in the Summer, the CTD profile is used to determine the depths of discrete positions in the thermal structure of the lake such as the mid-epilimnion. Trigger sample bottle at correct depths, while verifying the temperature profile (See Appendix B, Attachment A for a detailed list of monitoring stations and depths). Split Rosette Niskin samples into the required sample bottles/preservatives. An integrated sample³ is taken for phytoplankton, chlorophyll <i>a</i>, total suspended solids, particulate organic carbon, particulate nitrogen, particulate phosphorus, chloride, silica, total phosphorus, total dissolved phosphorus, and nitrate-nitrite, by compositing Niskin samples at various depths.

³For an unstratified water column, the integrated sample is prepared by taking equal volumes of water from SRF (1 m), 5 m, 10 m and 20 meters unless the depth is less than 20 meters. If the total depth is between 15 and 22 meters, the 20 meter sample is replaced by the bottom sample (B-1 or B-2). If the total depth is less than 15 meters, equal volumes are taken from surface, mid-depth, and bottom sample (B-1 or B-2). For a stratified water column, equal volumes are taken from the surface, 5 m, 10 m, and lower epilimnion (LEP). If the epilimnion is very shallow, equal volumes are taken from a maximum of four sampling depths and a minimum of two sampling depths. The underlying strategy is to collect a representative sample from the epilimnion.

Sample Type	Sampling Strategy
Zooplankton samples/ Secchi readings	<ul style="list-style-type: none"> • Conduct the 20 meter and B-2/100m vertical tows • Rinse the net • Pour into bottles and transfer to onboard laboratory for preservation • After tows are completed, measure transparency using the Secchi disk.
Benthos	<ul style="list-style-type: none"> • Collect four ponar grab samples at each benthos stations during the summer surveys and three Ponar grab samples at each station in the spring surveys. • During the summer survey, use one of the four grabs off for physical measurements and the remaining three for benthos analysis. (Physical measurements are not collected from benthos samples during the Spring surveys.)
Dissolved Oxygen	<ul style="list-style-type: none"> • During summer surveys, when the lakes are stratified, collect samples for DO determination at each master station in each lake. Record a full SeaBird profile DO. In addition, the surface and B-2 sample is used for duplicate analysis by Winkler titration. Simultaneously, analyze an oxygen-saturated sample, either from a sampled same depth or from the reagent water system, by Winkler titration.

Note: A separate dissolved oxygen survey is conducted in the Lake Erie Central Basin. See Appendix D, *Dissolved Oxygen and Temperature Profiles for the Central Basin of Lake Erie QAPP*, for detailed information regarding this survey.

Table 7-3 summarizes the types of samples (grab vs. composite), type of field QC, and parameters sampled at each depth.

Table 7-3. Sampling depth strategy for target parameters

Parameter Group	Sampling Depths	Sample Type
Total Suspended Solids, Particulate Organic Carbon, Particulate Nitrogen, Particulate Phosphorus	Integrated Sample Deep Chlorophyll Layer	Composite Grab
Chloride, Silica, Total Phosphorus, Total Dissolved Phosphorus, Nitrate + Nitrate	Surface Mid-depth Mid-epilimnion Lower epilimnion Thermocline Deep Chlorophyll Layer Upper hypolimnion Mid-hypolimnion Discrete Depths* B-10 B-2, B-1 Integrated	Grab Grab Grab Grab Grab Grab Grab Grab Grabs Grab Grab Grab Composite
Board Chemistry (Alkalinity, pH, Turbidity and Conductivity)	Surface Mid-depth Mid-epilimnion Lower epilimnion Thermocline Upper hypolimnion Mid-hypolimnion Discrete Depths* B-10 B-2, B-1	Grab Grab Grab Grab Grab Grab Grab Grabs Grab Grab
Winkler DO	Surface B-1	Grab Grab
Zooplankton	Tow 20 m to surface Tow B-2 to surface or from 100 m to surface, whichever is less	Integrated Integrated
Benthos	Sediment	Grab
Phytoplankton	Integrated Sample Deep Chlorophyll Layer	Composite Grab
Chlorophyll <i>a</i>	Surface Mid-depth B-2, B-1 Integrated	Grab Grab Grab Composite

* Discrete depths include 5 m, 10 m, 20 m, 30 m, 40 m, 50 m, 100 m and 200 m (as station depth allows)

NOTE: A suite of physical parameters, such as specific conductance and temperature, also are monitored with the SeaBird CTD (see section 8.1 and LG302, *Operating the SeaBird CTD*).

8.0 SAMPLING METHOD REQUIREMENTS

The primary data quality objectives when sampling are to:

- Collect representative samples at the *locations* described in Sections 7.1

- Collect representative samples at the *depths* described in Section 7.2
- *Preclude contamination* from the equipment and sample handling processes
- Verify that the sampling techniques yield reproducible results by collecting field duplicate samples from each basin and field blanks from approximately 25% of the stations sampled in each survey.

Station Locations: GLNPO will use a digital global positioning system (GPS) to ensure that sampling is conducted at the designated station locations. GPS is a satellite-based radio-navigation system developed and operated by the U.S. Department of Defense (DOD). It permits land, sea, and airborne users to determine their three-dimensional position, velocity, and time 24 hours a day, in all weather, anywhere in the world and is accurate within 25 feet. The same digital GPS system used on the bridge is connected to the SeaBird so that consistent readings are made at each location. When the *R/V Lake Guardian* arrives on station, the Captain will notify survey participants of the station name and ship time so that sample collection can begin. **Note:** For surveys in Lake Erie, sampling locations should sometimes be revisited due to windy conditions that can stir up the lake bottom. The Chief Scientist should review the results of turbidity measurements for Lake Erie to determine if another sampling event should be conducted on the return trip through the lake. If the turbidity is more than 3.5 NTU for any Lake Erie station, the results may be artifacts of sediment resuspension and may not accurately reflect conditions of the water column. In these cases, the Chief Scientist will, if possible, collect additional samples for the full suite of analyses during the return trip through Lake Erie.

Sampling Depths: Samples are collected at all stations at a series of depths. The exact depths are determined by the type of station (master and non-master), the season of the survey, the station depth, and the thermal profile. A generalized list of the samples collected is provided in LG 200, Table 1. Attachment A to this QAPP further details the sampling depths at the various stations. Prior to the survey, labels and other paperwork are prepared designating the sampling depths for the different stations. Once on station, depths will be determined using the CTD to define the temperature profile. During unstratified conditions that occur in the Spring, most of the sample depths are constant, however, the CTD profile is used to determine whether inverse stratification is present and sample accordingly. During stratified conditions that occur in the Summer, the CTD profile is used to determine the depths of discrete positions in the thermal structure of the lake such as the mid-epilimnion. The Chief Scientist or Shift Supervisor and the Rosette operator will interpret these readings and determine the depths of samples to be collected.

Further information on sample depth selection can be found in the WQS manual LG200, *Field Sampling Using the Rosette Sampler*, which includes a figure that illustrates an example thermal profile.

Controlling Contamination: Concentrations of chemicals in lake water are very dilute. A small amount of sample contamination can have a large effect on the results. Avoiding contamination is, therefore, a major goal of the Water Quality Surveys QA program. To reduce contamination from atmospheric dust, empty bottles will be capped during preparation from sampling. Care also should be taken in the storage of bottles to reduce exposure to “dirty” environmental conditions. The Niskin bottles used on the Rosette sampling device are opened as the device is dropped. This has the effect of flushing the bottles with thousands of gallons of water and effectively rinses the bottles clean of any carryover from previous sampling activities. Historical data has confirmed the effectiveness of this approach. As described below, samples collected in Niskin bottles with the Rosette device are transferred to pre-rinsed 500 mL brown and 1 gallon clear polyethylene containers (PEC) when the device is brought back on ship. Aliquots are then processed (filtration and preservation) from the 1 gallon containers for storage in 125 mL bottles for nutrient determination. Techniques to control sources of contamination during these field activities are described in Table 8-1.

Table 8-1: QA Techniques to Control Contamination During Field Sampling Activities

Contamination Source	Control Strategy
Sampling Equipment/ Bottles	<ul style="list-style-type: none"> • Open Niskin bottles as Rosette is lowered • Use new PEC containers to hold the sample for onboard analyses and laboratory preparations • Rinse each PEC bottle with sample before filling the container.
Atmospheric	<ul style="list-style-type: none"> • Cap empty bottles during all on-site activities (except actual collection or transfer of sample) • Store bottles in clean environments (e.g., avoid exhausts, dirt, dust, organic vapors, etc.) • Replace bottle caps immediately after adding preservative or, for those that do not require preservation, immediately after transfer to the permanent containers • Avoid repeated transfer of samples from one container to another • Perform sample preservation and filtration activities in the ship laboratory
Preservatives	<ul style="list-style-type: none"> • Use automatic pipettes or dispensers when adding preservative • Confirm that preserving agent has the same colored tags as that used on the sampling bottle. Investigate/implement corrective actions if mismatch occurs. • “Set up” dissolved oxygen samples immediately (see Section 9.1)
Filtration	<ul style="list-style-type: none"> • Use pre-cleaned filters that are stored in a contaminant-free environment

Specific sampling methods to be used in the Surveys are detailed in *Sampling and Analytical Procedures for GLNPO's Open Lake Water Quality Survey of the Great Lakes* (updated regularly, maintained onboard the *R/V Lake Guardian* during each cruise, and available from GLNPO). Sampling requirements also are described in the QAPPs prepared by the GLAS contractor, the biology grantee, and other organizations tasked with implementing sampling activities that support the Water Quality Surveys. Key requirements from these documents are highlighted below.

8.1 Sampling with the Rosette

A 12-bottle Rosette sampler system (SeaBird Electronics Carousel Water Sampler) is used to collect water samples for the following Survey parameters:

- all nutrient parameters
- phytoplankton
- chlorophyll *a*
- dissolved oxygen
- temperature
- total suspended solids
- turbidity
- specific conductance
- pH

The Rosette sampling system consists of an A-frame structure, 1000 feet of multi-conductor cable, a variable speed winch, a SeaBird Electronic Deck Unit with attached computer, a conductivity, temperature, and depth (CTD) sensor, an optical transmission sensor, a sensor for measuring photo-synthetically active radiation, a fluorometer with filters for chlorophyll detection, a pH electrode, and a dissolved oxygen sensor attached to the end of the cable. The sampling system allows an operator to remotely actuate a sequence of up to twelve 8-liter Niskin sampling bottles. The bottles can be closed

remotely from the deck in any pre-determined order while the array is submerged at various sampling depths.

The CDT measures water depth and temperature, which are graphically displayed onboard the research vessel. Sampling depth is detected by a pressure transducer on the CTD. To ensure that the display parameters are set to include the entire water column, the bottom sounding will be compared to the Rosette sample reading at each station. The Rosette winch operator obtains a depth sounding from the bridge and documents this on the Rosette form, then adjusts the computer program parameters, controlling the depth range to be displayed. The Rosette sampler is then lowered to the bottom at between 0.5 and 1 meter/second.

- If the bottom sensor is operational the Rosette is lowered to 1-2 meters from the bottom, and sampling may commence.
- If the bottom sensor is not providing usable results, the Rosette is lowered so that it touches the bottom and is then raised at least five meters from the bottom. In this case, the operator waits at least three minutes to allow the sampler to drift away from the disturbed area before dropping the Rosette back down to the B-2 (two meters from the bottom) depth for sampling.
- When the Rosette is lowered into the water, the Chief Scientist and marine technicians monitor the sampler to maintain a vertical cable. If the cable moves off vertical, the Chief Scientist and the ship Captain coordinate in an attempt to maneuver the ship to maintain a vertical cable. The ship GPS system provides a constant indication of distance off station. The final location is recorded in the Captain's log and in the hard-copy forms. (As per Section 8.3 below, benthic samples should always be collected within 50 meters of the station location.)

Samples are taken at each of the depths discussed in Section 7.2 as the Rosette is raised. Duplicate samples are taken sequentially at the randomly-determined duplicate sites and depths. (Duplicate sampling locations and depths in each basin are selected by the Chief Scientist for Board Chemistry prior to each survey using a random numbers generator.)

Additional details regarding required Rosette sampling procedures are given in GLNPO SOP LG200, *Field Sampling Using the Rosette* and SOP LG301, *Operating the SeaBird 25*.

8.2 Zooplankton Sampling Tows

Two sampling tows will be performed at each station. The first tow is done from 20 meters below the water surface using a 63 μm net. The second tow is a 'full' water column tow, from 2 meters above the bottom of the lake or 100 m, whichever is less, using a 153 μm net. If the station depth is less than 20 m, both tows should be taken from one meter above the bottom. *Triplicate tows are made at each of the master stations to provide QC samples.* **Note:** Due to the limited number of organisms in Lake Superior, two tows must be done with the 63 μm net for the 20 m sample and combined into one bottle. The 100 m tow is performed as in the other Lakes.

The tow net, with a screened sample bucket attached to the bottom, is lowered to the desired depth, and raised at a constant speed to collect zooplankton from the water column. The net is rinsed to free organisms after being lifted out of the water. The sample is concentrated into the sample bucket and is transferred to a pre-labeled 500 mL sample bottle. After zooplankton tows have been completed, transparency measurements are made using Secchi disks. **Note:** Secchi depth measurements are made only for tows performed during daylight hours (e.g., more than one hour after sunrise and more than one hour before sunset) and on the shady side of the boat, out of direct sunlight.

Additional details regarding sampling methodology for zooplankton are given in GLNPO SOP LG402, *Zooplankton Sample Collection and Preservation and Secchi Depth Measurement Field Procedures*.

8.3 Benthic Invertebrate Sampling Methods

Three separate samples of benthic invertebrates are taken with a Ponar grab sampler at each designated sample station and each of the three samples is processed, preserved, and stored separately. During the spring surveys, samples are taken at five sites: Saginaw Bay, 2 in Green Bay, and 2 in the Western Basin of Lake Erie and are analyzed specifically for the mayfly *Hexagenia*. During the summer surveys, all stations are sampled and analyzed for all benthic invertebrates. During the summer cruise, a fourth Ponar sample is taken for grain size and chemical analysis.

Samples are collected by lowering the Ponar to the sediment surface, in accordance with procedures outlined in GLNPO SOP LG406, *Benthic Invertebrate Field Sampling Procedure*. The sampling device is then raised to the deck where the sample is emptied into a plastic bucket. The sediment and animals are rinsed from the top screen and the interior of the Ponar. Rinsing is done at very low pressure to avoid damaging the organisms.

All of the survey sampling stations are located in depositional areas, so the bottom surface should be soft enough for sampling. If, however, the Ponar comes up empty, it is likely that the bottom substrate is hard packed clay, sand, or bedrock. In such cases, the station should be relocated to deeper water (moving as short a distance as possible) and the procedure repeated. If problems persist, the GLNPO Chief Scientist must be consulted immediately to determine if sampling should be discontinued at the station, and if the station location should be revised for the next survey. **Note:** The vessel should stay within 50 meters of the station location for benthic sampling because benthic sites are typically near shore, and sites greater than 50 meters away may be non-depositional zones.

If the samples contain large amounts of sand, zebra mussel shells, or other debris that prevent sediment from quickly passing through a 500 μ m mesh, the samples should be elutriated using the procedures given in GLNPO SOP LG406.

8.4 Meteorological Methods

The ship officer in charge of the bridge (the bridge officer) is responsible for recording wind speed and direction, wave height and direction, air temperature, barometric pressure, visibility, present weather conditions, and heading (when underway). These recordings are made each hour, on the hour, and are recorded in the ship's log. In addition, the officer in charge is responsible for recording the time and description of any unusual event (e.g., man overboard).

At each station, the bridge officer also is responsible for recording the station identification number, arrival time, departure time, wind speed and direction, wave height and direction, barometric pressure, water depth, surface water temperature, air temperature, geographic location (loran and/or GPS), and final location (if vessel has drifted during sampling). This information is recorded in the Captain's log, which yields carbon copies that are provided to GLNPO at the conclusion of the surveys.

Collection of meteorological data will be conducted in accordance with GLNPO SOP LG300, *Meteorological Data Aboard the R/V Lake Guardian*.

9.0 Sample Handling and Custody Requirements

Once the Rosette is brought on deck, samples are immediately aliquotted, filtered, and preserved as described in Sections 9.1 through 9.5 and detailed in corresponding SOPs. Samples are labeled as described in Section 6. Formal chain of custody procedures are not required for the surveys.

Table 9-1 summarizes sample preservation and holding times for survey parameters. All survey samples collected during the Water Quality Surveys must be preserved in accordance the requirements summarized in this table and detailed in the corresponding SOPs. For samples that are shipped frozen to laboratories, a frozen solution of ethanol can be used where dry ice is not available.

9.1 Rosette Sample Handling

After the Rosette is brought on deck, aliquots are immediately transferred from the Niskin bottles into appropriate containers for each type of analysis. Sample collection and transfer is performed by the Chief Scientist (or Shift Supervisor) with assistance from contractor, or occasionally, grantee staff. Staff performing these operations wear latex gloves to preclude contamination of the samples during handling. They rinse each cubitainer or polyethylene bottle with sample drawn from the Niskin bottles before filling. Sample rinsing is performed by removing the container cap, partially filling the bottle with sample, capping the container, and shaking to ensure the entire surface is flushed with sample. The cap is then removed and the rinse poured out prior to filling the container.

Aliquots for nutrients, pH, conductivity, alkalinity, turbidity: Aliquots are transferred from the Niskin bottles to pre-labeled 1 gallon polyethylene cubitainers on deck. The cubitainers are pre-labeled to minimize transcription errors. Cubitainer caps also are pre-labeled with the same sample number. This provides a backup means of identifying the sample if the label comes off the container. After collecting the sample in the 1 gallon cubitainer, the cubitainer is taken to the ship laboratory for sample preservation and storage according to the scheme described in Table 9-1 pending analysis by the GLAS contractor (nutrients) or the board chemist (pH, specific conductance, alkalinity, turbidity). In the laboratory, nutrient samples are processed according to the procedures in the WQS manual, LG212, *SOP for Nutrient Samples Processing*.

Aliquots for chlorophyll a: The chlorophyll *a* aliquots are transferred directly from the Niskin bottles into 300 mL brown polyethylene bottles while on deck. Once transferred, they are immediately sent to the onboard lab for filtration and preservation. The entire filtration and preservation procedure is carried out as much as possible in subdued light (green) to prevent photodecomposition. Samples are treated with a MgCO_3 solution during filtration to eliminate acid-induced transformation of chlorophyll to its degradation product, pheophytin. Filtration is ideally performed within 30 minutes of collection by vacuum filtration at <5 psi. (Though less desirable, filtration may be delayed as long as 2 hours without compromising survey results.) The filter is stored in darkness in a capped glass tube. The filtered samples are grouped by station and completely wrapped in aluminum foil during storage and transport to the land-based GLAS laboratory. The samples are stored in a freezer pending transfer to the GLAS lab, and during transit, are stored in a cooler containing dry ice.

Dissolved oxygen aliquots: During the Lake Erie surveys and at master stations, aliquots for dissolved oxygen are immediately transferred from selected Niskin bottles by inserting an 8 to 10 inch length of flexible plastic Tygon tubing connected to the Niskin bottle outlet plug into the bottom of a 60 mL glass BOD bottle. Flow will be regulated by the outlet plug so as to minimize turbulence and mixture of oxygen with the sample. The BOD bottle is filled to overflowing, allowing overflowing to continue five seconds before adding, in series, the first two reagents, allowing the floc to settle, mixing, and allowing floc to settle again. The dissolved oxygen sample analyses are then completed in the main laboratory. (This procedure is used to calibrate/verify the dissolved oxygen readings collected from the SeaBird.)

Integrated composite samples for phytoplankton, chlorophyll a, particulate nitrogen, particulate phosphorus, particulate organic carbon, and total suspended solids and nutrients (chloride, silica, total phosphorus, dissolved phosphorus, and nitrate/nitrite): For an unstratified water column, the integrated sample is prepared by taking equal volumes of water from SRF (1 m), 5 m, 10 m and 20 meters unless the depth is less than 20 meters. If the total depth is between 15 and 22 meters, the 20 meter sample is replaced by the bottom sample (B-1 or B-2). If the total depth is less than 15 meters, equal volumes are

taken from surface, mid-depth, and bottom sample (B-1 or B-2). For a stratified water column, equal volumes are taken from the surface, 5 m, 10 m, and lower epilimnion (LEP). If the epilimnion is very shallow, equal volumes are taken from a maximum of four sampling depths and a minimum of two sampling depths. The underlying strategy is to collect a representative sample from the epilimnion. (see Section 7.2). The 1 liter aliquots are transferred to a 1 gallon cubitainer to create a composite from the euphotic zone. Samples for phytoplankton analysis are preserved with 10 mL Lugol's solution (to a final concentration of 1%) and stored in the dark. *Note:* Due to the low number of organisms in Lake Superior, two 1 liter composite samples are collected for phytoplankton at each station.

9.2 Zooplankton Sample Handling

Zooplankton samples are collected and transferred to pre-labeled 500 mL sample bottles as described in Section 8.2 and immediately transferred to the biology lab onboard the ship for sample preservation. The organisms are narcotized with 20 mL soda water and allowed to stand for 30 minutes in the refrigerator before being preserved with 20 mL sucrose formalin solution.

9.3 Benthic Invertebrate Sample Handling

Samples for benthos determinations are brought to the ship board laboratory for preservation after being elutriated or sieved on deck. (Elutriation is rarely, if ever, required during the surveys.) The samples are preserved in the lab with 50-100 mL of 37% buffered formaldehyde with Rose Bengal. The sample is then topped off with tap water and inverted 3 times before storage in the onboard walk in refrigerator. Samples for grain size and chemical analysis are stored unpreserved in the shipboard freezer.

Table 9-1. Sample Preservation Methods, Holding Times, and SOPs

Parameter	Maximum Unpreserved Sample Holding Time	Maximum Preserved Holding Time	Operational Storage Methods and Holding Time Limits	Preservation/ Storage Method	SOP Reference
Turbidity	not established	15 hours	2 hours, 12 hours if control standards are out (4°C)	Refrigerate (4°C)	LG200 or LG201*, LG500
Dissolved Oxygen	perform ASAP	none	1 st two reagents immediately. Add acid w/in 8 hours. Titrate w/in 30 minutes of acid addition	not applicable	LG301, LG303, LG304; LG200 or LG201*, LG501
Specific Conductance	unstable	15 hours	2 hours, 12 hours if control standards are out (4°C)	Refrigerate (4°C)	LG200 or LG201*, LG301, LG500
pH	unstable	15 hours	2 hours, 12 hours if control standards are out (4°C)	Refrigerate (4°C)	LG200 or LG201*, LG301, LG500
Alkalinity	unstable	15 hours	2 hours, 12 hours if control standards are out (4°C)	Refrigerate (4°C)	LG200 or LG201*, LG500
NO ₃ -NO ₂	24 hours	3 months	2 hours at land-based lab <3 months	1 mL H ₂ SO ₄ /L in filtered sample	LG200 or LG201*, LG203, LG212
Total Dissolved Phosphorus	24 hours	3 months	2 hours at land-based lab <3 months	1 mL H ₂ SO ₄ /L in filtered sample	LG200 or LG201*, LG204, LG212
Total Phosphorus	24 hours	3 months	2 hours at land based lab <3 months	1 mL H ₂ SO ₄ /L in filtered sample	LG200 or LG201*, LG204, LG212
Chloride	not established	3 months	2 hours	Refrigerate (4°C)	LG200 or LG201*, LG205, LG212
SiO ₂	not established	3 months	2 hours at land-based lab <3 months	Refrigerate (4°C)	LG200 or LG201*, LG205, LG212

Parameter	Maximum Unpreserved Sample Holding Time	Maximum Preserved Holding Time	Operational Storage Methods and Holding Time Limits	Preservation/ Storage Method	SOP Reference
Particulate Organic Carbon, particulate organic nitrogen, particulate organic phosphorus, total suspended solids	filter ASAP	not established	not established	Frozen at -10°C	LG200 or LG201*, LG206, LG207, LG208, LG209, LG210, LG302
Dissolved Organic Carbon	filter ASAP	24 hours	filtered immediately and stored at 4°C	1 mL H ₂ SO ₄ /L	LG200 or LG201*, LG210, LG211
Chlorophyll <i>a</i>	30 minutes	approximately 3½ weeks if frozen (-20°C) in darkness	30 minutes unpreserved (ideal) 2 hours unpreserved (maximum)	filter w/ MgCO ₃ . Freeze in darkness.	LG200 or LG201*, LG404, LG405
Phytoplankton	1-2 hours	Several months if stored in the dark	2 hours until preservation	10 mL Lugol's fixative/L sample (store in the dark at 4°C) Formalin upon arrival at the laboratory	LG200 or LG201*, LG400, LG401
Zooplankton	1 hour Store at 4°C ASAP	unlimited	Narcotize and refrigerate immediately and not later than 1 hour after sample collection. Preserve 30 minutes later.	Narcotize with 20 mL soda water; let stand 30 minutes at 4°C; preserve with 20 mL sucrose/formalin solution	LG402, LG403
Benthic invertebrates	1-2 hours	unlimited	1 hour until preservation	50 to 100 mL 37% formaldehyde with Rose Bengal solution at 4°C	LG406, LG407
Sediment Samples for chemical and grain size analysis	Preserve ASAP	not established	1 to 2 hours	Freeze	LG406, LG600, LG601, LG602

* LG201 when Rosette is not operational.

10.0 ANALYTICAL METHODS REQUIREMENTS

10.1 Nitrate/Nitrite

Nitrate and nitrite forms of nitrogen are determined on grab and composite samples taken from the Rosette. (Sample preparation is conducted on board the *R/V Lake Guardian* as described in Section 9.1.) The analyses are performed in a land-based laboratory by the GLAS contractor, in accordance with GLNPO SOP LG203, *Nitrate-Nitrite in Lake Water, QuickChem FIA + 8000 Method*. Briefly, nitrate is quantitatively reduced to nitrite by passing the sample through a column containing copper coated cadmium. The nitrate (reduced nitrite plus original nitrite) is determined by diazotizing with sulfanilamide dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm.

10.2 Total Phosphorus and Total Dissolved Phosphorus

Total phosphorus and total dissolved phosphorus are determined on grab and composite samples taken from the Rosette and on sediment samples taken during the summer surveys. (Sample preparation is conducted on board the *R/V Lake Guardian* as described in Section 9.1.) The analyses are performed in a land-based laboratory by the GLAS contractor, in accordance with GLNPO SOP LG204, *Total and Total Dissolved Phosphorous (Lachat Method 10-115-01-1-F for QuickChem FIA+8000)*. In this procedure, samples are digested in the presence of sulfuric acid and persulfate to convert (hydrolyze) polyphosphate and organic phosphorous to orthophosphate. The orthophosphate ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form 12 molybdophosphoric acid. This complex is reduced with ascorbic acid to form a blue complex that absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

10.3 Chloride and Silica

Chloride and silica are determined on grab and composite samples taken from the Rosette. (Sample preparation is conducted on board the *R/V Lake Guardian* as described in Section 9.1.) The analyses are performed in a land-based laboratory by the GLAS contractor, in accordance with GLNPO SOP LG205, *Chloride and Silica in Lake Water (Lachat Method)*. In this procedure, thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. Free thiocyanate ion forms the highly colored ferric thiocyanate in the presence of ferric ion. The highly colored ferric thiocyanate absorbs strongly at 480 nm, producing a response that is proportional to the chloride concentration. The calibration curve is non-linear.

Soluble silica species react with molybdate under acidic conditions to form a yellow silica molybdate complex. This complex is subsequently reduced with 1-amino-2-naphthol-4-sulfonic acid (ANSA) and bisulfite to form a heteropoly blue complex that has an absorbance maximum at 820 nm.

10.4 Particulate Organic Carbon

Particulate organic carbon (POC) is determined on grab and composite samples taken from the Rosette. (Sample preparation is conducted on board the *R/V Lake Guardian* as described in Section 9.1.) The analyses are performed in a land-based laboratory by the GLAS contractor, in accordance with GLNPO SOP LG207, *Analysis of Particulate Phase Organic Carbon*. In this procedure, subsamples of the exposed glass fiber filters are placed into tin capsules and loaded into a Carlo Erba Elemental Analyzer 1108 equipped with an autosampling device. The elemental analyzer comprises a combustion furnace, GC oven, and thermal conductivity detector. Once loaded into the autosampler, the samples are automatically dropped in a vertical quartz reactor tube inside a 1000°C furnace. The temporarily oxygen-enriched carrier gas oxidizes the sample. Quantitative oxidation is achieved when the resulting mixture of

gases passes over a tungsten anhydride catalyst. The gas mixture then passes over the elemental copper where excess oxygen is removed and nitrous oxide is reduced to elemental nitrogen. The sample gases then pass through a packed chromatographic column to be separated, eluted, and detected by a thermal conductivity detector. Organic carbon is quantified by the external standard method.

10.5 Particulate Nitrogen

Particulate nitrogen is determined on integrated composite samples taken from the Rosette. (Sample preparation is conducted on board the *R/V Lake Guardian* as described in Section 9.1.) The analyses will be performed in a land-based laboratory by the GLAS contractor, in accordance with GLNPO SOP LG208, *Particulate-Phase Total Nitrogen by Alkaline Persulfate Oxidation Digestion (Lachat Method)*. In this procedure, nitrogen compounds are spontaneously oxidized to nitrate in alkaline persulfate when the media is autoclaved under 15 psi and 121°C. Nitrogen losses are not observed when oxidation occurs under these pressure conditions. Nitrate is quantitatively reduced to nitrite by passing the sample through a column containing copper coated cadmium. The nitrite (reduced nitrate plus original nitrite) is determined by diazotizing with sulfanilamide dihydrochloride. The resulting water soluble dye has a magenta color that is read at 520 nm.

10.6 Particulate Phosphorus

Particulate phosphorus is determined on the integrated composite samples taken from the Rosette. (Sample preparation is conducted on board the *R/V Lake Guardian* as described in Section 9.1.) The analyses are performed in a land-based laboratory by the GLAS contractor, in accordance with GLNPO SOP LG209, *Particulate-Phase Total Phosphorous by Persulfate Oxidation Digestion (Lachat Method)*. In this procedure, the filters are digested in the presence of sulfuric acid and ammonium persulfate to hydrolyze polyphosphates and organic phosphorous to orthophosphate. The orthophosphate ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form 12-molybdophosphoric acid. This complex is reduced with ascorbic acid to form a blue complex that absorbs light at 880 nm. The absorbance is proportional to the concentration of the orthophosphate in the sample.

10.7 Dissolved Organic Carbon

Dissolved organic carbon (DOC) will be determined on grab and composite aliquots from the Rosette sampling device. (Sample preparation is conducted on board the *R/V Lake Guardian* as described in Section 9.1.) The analyses are performed in a land-based laboratory by GLAS contractor staff in accordance with GLNPO SOP LG211, *SOP for Dissolved Organic Carbon*. Determination of organic carbon requires the removal of inorganic carbon which is present in the samples as carbonate. This is accomplished with an automated pre-treatment system in which a high velocity stream of organic-free air transforms the sample into a thin turbulent liquid film that is rapidly transported through a large bore coil that provides the necessary surface area for efficient removal of carbon dioxide. Up to 500 mg of inorganic carbon can be removed at a purge rate of 500 mL/minute with minimal loss of volatile organic compounds. An aliquot of the carbonate-free sample is then segmented and presented for analysis. The aliquot is mixed with a stream of acid and potassium persulfate and subjected to ultraviolet (UV) radiation. The resultant CO₂ generated from the organic carbon present in the sample is then purged with a stream of CO₂-free air or nitrogen and measured with a non-dispersive infrared analyzer. The dissolved organic carbon concentrations are calculated from peak heights generated by a chart recorder connected to the infrared analyzer.

10.8 Total Suspended Solids

Total suspended solids (TSS) concentrations are determined on integrated composite samples collected from the Rosette sampling device. TSS filtration is performed on board the ship by GLNPO scientists in accordance with GLNPO SOP LG302, *Sampling and Analysis of Total Suspended Solids in Lake Water*. Aliquots from each desired depth are poured from the Rosette and filtered under vacuum through a 47 mm diameter pre-weighed glass fiber filter. The suspended solids are retained on the filter and frozen at -10°C until final weighing by the GLAS contractor on an analytical balance in the contractor's land-based laboratory.

10.9 Specific Conductance, Total Alkalinity, Turbidity, and pH

Grab samples collected with the Rosette sampling device as described in Sections 8.1 and 9.1 are analyzed on board the *R/V Lake Guardian* by GLNPO scientists with assistance from the marine technicians. The equipment used for these analyses is standardized for each of these parameters at the beginning of each lake survey. Samples are analyzed in accordance with the procedures detailed in GLNPO SOP LG500, *Standard Operating Procedure for GLNPO Board Analyses*. Briefly, this procedure involves 1) placing a 250 mL sample on the specific conductivity apparatus and heating it with a 110 volt immersion heater to exactly 25.0°C. The conductivity reading is recorded, and the pH electrode is then placed in the sample. As soon as the pH meter indicates that the pH reading is stable, that reading is recorded, the beaker is removed from the apparatus, and the content is used to fill the turbidity cuvette and the 100 mL alkalinity flask. The content of the alkalinity flask is transferred to the alkalinity apparatus and titration is performed. The readings from the alkalinity titration and the turbidimeter are recorded on the board chemistry data forms.

pH measurements also are collected from the SeaBird using procedures described in the *QAPP Addendum to The Great Lakes Water Quality Studies of Lakes Michigan, Huron, Erie, Ontario, and Superior*. This QAPP is included as Appendix C to the Sampling and Analysis Manual for the Great Lakes Water Quality Surveys. Results are averaged every half meter and saved with the SEASAVE software program (described in the Appendix C QAPP) to convert the raw data files to graphic or tabular format. *Note:* The pH measurements taken off the SeaBird are primarily used, along with other SeaBird data, to define lake conditions and determine appropriate sampling depths. pH measurements collected from the SeaBird are not considered to be as reliable as those determined in the laboratory and are, therefore, not typically used by GLNPO for purposes other than depth selection.

10.10 Dissolved Oxygen

SeaBird Method: DO measurements are collected using the SeaBird in all lakes during the Summer surveys. During summer surveys, when the lakes are stratified, samples are collected for DO determination each master station in each lake. A full SeaBird profile is recorded for DO. In addition, a surface and B-2 sample will be collected and analyzed in duplicate by Winkler titration (see below). Simultaneously, an oxygen-saturated sample, either from a sampled same depth or from the reagent water system, will be analyzed by Winkler titration. The B-2 samples is collected only when the nepheloid layer is present. For monitoring stations in Lake Erie a B-1 sample is collected instead of the B-2. An additional DO survey is conducted in the central basin of Lake Erie. Refer to Appendix D, *Sampling and Analytical Procedures for GLNPO's Open Lake Water Quality Survey of the Great Lakes*, for DO and temperature profiles for this survey. Detailed procedures for operating the SeaBird can be found in Appendix D and also in SOP LG200, *Field Sampling Using the Rosette Sampler*.

Winkler Method: Dissolved oxygen is measured on water samples from selected depths in Lake Erie at each station on the summer survey, and from the master stations on the other lakes. Analysis of these samples is made by the azide modification of the Winkler test. The sample is sequentially treated with manganous sulfate, a potassium hydroxide/potassium iodide solution, and sulfuric acid. The initial

precipitate of manganous hydroxide combines with the dissolved oxygen to form a brown precipitate, manganic hydroxide. Upon acidification, the manganic hydroxide forms manganic sulfate, which acts as an oxidizing agent to release free iodine from the potassium iodide. The iodine, which is stoichiometrically equivalent to the dissolved oxygen in the sample is then titrated with sodium thiosulfate. These analyses are performed to calibrate/verify the SeaBird readings.

10.11 Phytoplankton

Phytoplankton identification and biovolume are determined on the integrated sample (a composite of the epilimnion in stratified conditions and in unstratified conditions a composite of several upper depth samples, see Section 7.2) collected at each site using the Rosette sampling device and also on an additional sample from the deep chlorophyll layer (DCL) during Summer surveys. Analysis is performed by grantee staff in a land-based laboratory in accordance with GLNPO SOP LG 401, *Phytoplankton Analysis*. The method, called the Modified Utermohl method, involves the microscopic examination of a preserved water sample. Initially, a preliminary scan is made to determine the volume of sample needed for all portions of the procedure. A settled sample of appropriate volume is then examined at a magnification of 500x for non-diatom algae and Urosolenia species (hereafter referred to as 'soft algae'). A second examination is performed on a cleaned diatom preparation for identification and enumeration at a magnification of 1250x. The soft algae portion of the settled phytoplankton samples are examined and analyzed using an inverted microscope (Leitz Diavert or equivalent microscope). During examination of the settled sample, most diatoms are enumerated and identified only as live pennates, empty pennates, live centrics, and empty centrics, with the only exception being species of Urosolenia (=Rhizosolenia). Actual species identification of diatoms (excluding Urosolenia) and cell volume measurements are done under oil immersion (1250x) by another method. While not included in the regular counts, note should be made of the presence of other identifiable species. Diatoms should be identified and enumerated at 1250x. Identification should be down to the lowest taxonomic rank possible. Results for the sample sedimentation procedure are reported as cells per mL. Biovolume is calculated using formulas representing the closest approximation of geometric shape. The data from the diatom slides is reported as percent composition of the 1250x count. This percent is applied back to the live diatom counts at 500x to determine a cells/mL count for each species.

10.12 Zooplankton

Zooplankton biomass and identification are performed by grantee staff in a land-based laboratory in accordance with GLNPO SOP LG 403, *Zooplankton Analysis*. The method is a microscopic examination of a preserved zooplankton sample collected from the conical tow nets. Microcrustacea are examined in four stratified aliquots under a stereoscopic microscope. Rotifera are examined in two equal volume sub-samples under a compound microscope. Four sub-samples are examined and enumerated. All microcrustaceans are identified and enumerated under a dissecting microscope. Rotifers and nauplii also are counted but only from the tow taken with the 63 mm mesh net. Tows taken with the larger mesh (153 mm) will not capture sufficient numbers of the smaller rotifers. All rotifers, microcrustacean nauplii and Dreissena veligers and post-veligers are identified and enumerated under a compound microscope at 100x magnification.

10.13 Chlorophyll a

Chlorophyll *a* determinations are made by grantee staff in a land-based laboratory in accordance with GLNPO SOP LG 405, *In vitro Determination of Chlorophyll a in Freshwater Phytoplankton by Fluorescence*. Chlorophyll-containing phytoplankton in a measured volume of sample water are concentrated onto a glass fiber filter by low vacuum filtration. After sonication, pigments are extracted in a 90% buffered acetone solution for 16 to 24 hours at -20°C. The extracted slurry is removed by filtration, and the fluorescence of the extract is read using a digital fluorometer. The concentration in the

natural water sample is reported in µg/L.

In situ chlorophyll measurements also are made from the SeaBird and averaged every half meter. Data are saved in the SEASAVE program as described in the *QAPP Addendum to The Great Lakes Water Quality Studies of Lakes Michigan, Huron, Erie, Ontario, and Superior*.

10.14 Benthic Invertebrates

Benthic invertebrates are identified and enumerated by grantee staff in a land-based laboratory in accordance with GLNPO SOP LG 407, *Benthic Invertebrate Laboratory Procedure*. Prior to analysis, they are rinsed to remove the formalin. The rinsed sample is spread on a gridded 500 mm mesh bottomed, stainless steel pan and subsampled using a 30-sided die or a random numbers table and a grid-sized cookie cutter. One or more subsampled grids are transferred to a smaller container where individual organisms can be examined under a dissecting microscope. Samples are sorted according to type and counted as sorting occurs.

10.15 Meteorology Measurements

Meteorological measurements are collected on the bridge, as described in Section 8.4 and GLNPO SOP LG 300, *Meteorological Data Aboard the R/V Lake Guardian*.

11.0 QUALITY CONTROL REQUIREMENTS

GLNPO implements several types of field and laboratory QC measures to monitor and control the quality of all data gathered from water column and sediment samples. These measures are used to identify and correct problems as they occur and to define the quality of the data generated for the surveys. The specific types of QC measures employed vary according to the sample collection process, the measurement process, and the location of the analytical laboratory. The QC sample requirements are provided in each analytical SOP in the WQS manual. For many parameters, a field duplicate, lab duplicate, and field reagent blank are collected with each group of 3, 4, or 5 stations depending on the lake. A Random Number Generator (RNG) is used to determine the stations and depths of these QC samples. Where basins are well defined, at least one of each is collected from each basin. In general, QC measures include one or more of the following:

- *Field duplicates or field replicates* are used to verify that the entire sampling and analysis process is capable of yielding reproducible results. These duplicates also can be used to develop quantitative estimates of imprecision associated with field and analytical activities. Field duplicates are collected for the nutrients and many of the all total and dissolved parameters collected off the Rosette sampling device (except for the integrated composite samples), and field triplicates are collected for all benthos samples at all stations and for all zooplankton tows at the master stations. Field duplicates also are collected for Secchi disk measurements whenever a field duplicate is collected for a sample collected at 1 meter below the surface. Performance criteria for these field duplicates are given Table 11-1. These performance criteria are under ongoing review and can change following re-evaluation. The performance criteria also are listed in each SOP in the WQS manual.
- *Lab duplicates or lab splits* are used to verify that the laboratory measurement process is capable of yielding reproducible results. These duplicates also can be used to develop quantitative estimates of imprecision associated with analytical activities. This measure primarily serves to identify and correct problems as they occur so that overall data quality objectives for the surveys are not compromised. Lab duplicates are performed on all nutrient, many physical, and biological parameters analyzed by the GLAS contractor and biology grantee. For most

measurements except the particulate nutrients, the lab duplicate can be used in combination with the field duplicate to separate sources of field and lab error. (True field duplicates are not collected for the particulate nutrients.) Also, lab duplicates are not performed on the board chemistry parameters because the field duplicates serve to capture the same information. Performance criteria for required lab duplicates are given in Table 11-2. These performance criteria are under ongoing review and can change following re-evaluation.

- *Laboratory Check Standards* are used to verify that the laboratory procedures and systems are in control for all physical and chemical measurements (standards do not exist for phytoplankton, zooplankton, and benthos). These check standards also can be used to develop quantitative estimates of bias associated with analytical activities. Generally, these include a high concentration check standard (CH) to verify that the process is yielding accurate measurements at the upper end of the measurement range, and a low concentration check standard (CL) to verify the process yields accurate results at the lower end of the measurement range. Both standards are treated as much like field samples as possible to reflect laboratory procedures. (These standards do not reflect field operations such as filtration and transfer from the cubitainer to the sample storage bottle.) Bias limits, defined in terms of absolute or percent differences from the ‘true’ concentration’ are given in Table 11-3. Precision also can be tracked over time by maintaining control charts of all lab check standard analyses and calculating the standard deviation of these analyses. The precision and bias results can be used to quantify the accuracy of the measurement process.
- *Lab spiked field samples* (also known as matrix spike samples) are used to evaluate how well the laboratory and method procedures are recovering the target parameters from the sample matrix. These spiked samples also can be used to develop quantitative estimates of bias associated with analytical activities. In the water quality surveys, such tests are performed for particulate nitrogen and particulate phosphorous at a frequency of 1 matrix spike per 40 samples. Accuracy limits for these spikes are given in Table 11-4.
- *Reagent blanks* (also known as method blanks) are used to characterize the effects of contamination that might be introduced by laboratory processes and systems (reagents, instruments, atmosphere, etc.) on sample results. Such blanks are analyzed for many physical and chemical measurements except the board parameters (field blanks capture any required information concerning contamination about the board parameters). Reagent blanks are not created and analyzed for phytoplankton, zooplankton, or benthos samples because the possibility of contaminating samples with these parameters is minimal to non-existent. Performance criteria for laboratory reagent blanks that are required in the surveys are given in Table 11-5.
- *Field blanks* are used to characterize the effects of contamination that might be introduced during either the sampling, sample handling, sample transport, or laboratory analysis processes on sample results. One field blank is collected from each basin (where basins are well-defined) to demonstrate the absence of contamination during the Rosette sampling, sample transfer, sample preservation and storage process. Field blanks are not collected for the phytoplankton, zooplankton, or benthos because the logistics involved in collecting such a sample are not warranted by the remote possibility of contaminating samples with these parameters. Table 11-6 gives performance criteria that will be applied to all field blanks collected during the Water Quality Surveys.

In addition, for the turbidity determination, the formazin calibration standard is prepared prior to each survey and checked at least once prior to each cruise.

Analysts must compare analytical results to the performance criteria listed in the pertinent SOP to identify

QC failures. If the results are outside the acceptance criteria, the analyst should first review their calculations for errors and if none are identified, they must follow the corrective action procedures listed in each SOP. Corrective action procedures will often be handled at the bench level by the analyst, who reviews the preparation or extraction procedure for possible errors, checks the instrument calibration, spike and calibration mixes, instrument sensitivity, and any other potential sources of error. If failure occurs and an error is identified, the analyst should re-run quality control and RFS samples in the entire analytical batch to confirm the results. Because analysis of field duplicates and lab duplicates usually occurs after leaving a specific station and re-sampling is largely impossible, re-analysis of these samples to confirm results may be the limit to corrective actions when all other QC samples within a batch meet acceptance criteria. For analyses conducted onboard, if the problem persists or cannot be identified, the matter must be referred to the Chief Scientist for further investigation. Depending upon the Chief Scientist's evaluation, the analyst may or may not be required to prepare and re-run the samples. Once a decision is made, full documentation of the corrective action procedures and assessment of the final result must be filed with the WQS QM Technical Lead (Marvin Palmer) or the GLNPO QM. For analyses conducted at contract or grantee laboratories, this information can be included with submitted data. When contractor or grantee laboratories have a question regarding acceptable corrective actions, they should contact the Biology Technical Lead or Limnology Technical Lead as appropriate for instruction at a time when corrective action can still be taken.

Table 11-1. Method Performance Criteria - Overall Precision Measures

Description	Survey Parameter	Minimum Frequency	Performance Criteria
Relative percent difference between field duplicates (Measures precision of sampling, transport, and analysis procedures-also referred to as system precision)	Chloride Nitrate + Nitrite Silica	One per basin	Relative Percent Difference \leq 20%
	Total Dissolved Phosphorus Total Phosphorus	One per basin	Difference \leq 2.0 $\mu\text{g/L}$
	Alkalinity	One per basin	Difference $<$ (1 + 0.01 x mean reading) mg/L
	pH	One per basin	Difference $<$ 0.3 SU
	Turbidity	One per basin	Difference $<$ (0.1 + 0.1 x mean reading) NTU
	Conductivity	One per basin	Difference $<$ 2.0 $\mu\text{mhos/cm}$
	Dissolved Organic Carbon Particulate Phosphorus Particulate Organic Carbon Particulate Nitrogen Total Suspended Solids	None	Samples are filtered in duplicate on ship. See Table 11-2
	Phytoplankton Dissolved Oxygen - Winkler Method	None	—
	Zooplankton	Master stations collected in triplicate for each net mesh size	Relative Standard Deviation criteria under consideration
	Secchi Disk Measurement	Every time a field duplicate of the Surface sample is collected	Difference \leq 0.5 meter; two different analysts should take the duplicate measurements
	Chlorophyll <i>a</i>	One per batch	Relative Percent Difference \leq 25% (interim limit)*
	Benthos	100% of samples collected in triplicate	Relative Standard Deviation criteria under consideration
	Meteorology	Not required	Not applicable

* Interim Limit = These limits will be used until there is enough data to calculate performance limits for this procedure.

Table 11-2. Method Performance Criteria - Lab Precision Measures

Description	Survey Parameter	Minimum Frequency	Performance Criteria
Relative percent difference of lab duplicates Measures lab precision	Total Dissolved Phosphorus Total Phosphorus	One per basin	Difference $\leq 2.0 \mu\text{g/L}$
	Chloride Nitrate + Nitrite Particulate Phosphorus Particulate Nitrogen Particulate Organic Carbon Dissolved Organic Carbon Silica	One per basin	Relative Percent Difference $\leq 20\%$
	Total Suspended Solids	At least once during the sampling of each Great Lake	$\pm (0.2 \text{ mg/L} + 0.2 \times \text{mean})$
	Phytoplankton	10% of samples are analyzed by a second analyst	Bray-Curtis Index of 60 (interim limit)*
	Zooplankton	10% of samples are analyzed by a second analyst	Percent similarity of 90% (see LG403 for calculations)
	Chlorophyll a	One per batch	Relative Percent Difference $\leq 25\%$ (interim limit)*
	Benthos	10% of samples	Identification corroborated by second analyst; $< 10\%$ difference (with special consideration for samples with very low numbers of individuals)
	Dissolved Oxygen - Winkler Method	Each Master station	Absolute difference $\leq 0.2 \text{ mg/L}$
		DO Surveys: All SRF and B-1 samples	
	Alkalinity Conductivity Meteorology pH Turbidity	None	—

* Interim Limit = These limits will be used until there is enough data to calculate performance limits for this procedure.

SRF = Surface (one meter below the surface)

B-1 = Bottom (station depth) minus one meter

Table 11-3. Method Performance Criteria - Lab Bias Measures**

Description	Survey Parameter	Minimum Frequency	Performance Criteria
Lab Check Standards (standard solutions analyzed at one or more concentrations to verify that laboratory processes are in control) and other comparisons (Measures lab bias)	Nitrate + Nitrite	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	Accuracy (mg/L): High Check Standard: 0.60 ± 0.09 ; Low Check Standard: 0.20 ± 0.03
	Total Dissolved Phosphorus Total Phosphorus	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	Accuracy ($\mu\text{g/L}$): High Check Standard: 15.0 ± 3.0 ; Low Check Standard: 3.0 ± 2.0 (interim limit)*
	Chloride	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	Accuracy (mg/L): High Check Standard: 17.3 ± 1.2 ; Low Check Standard: 5.6 ± 0.6
	Silica	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	Accuracy (mg/L): High Check Standard: 0.467 ± 0.053 ; Low Check Standard: 0.093 ± 0.018
	Particulate Organic Carbon	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	Accuracy ($\mu\text{g/L}$): High Check Standard: 80.0 ± 16.0 ; Low Check Standard: 5.0 ± 3.0
	Particulate Nitrogen	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	Accuracy (mg/L): High Check Standard: 1.20 ± 0.12 ; Low Check Standard: 0.40 ± 0.04
	Particulate Phosphorous	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	Accuracy ($\mu\text{g/L}$): High Check Standard: 120.0 ± 12.0 ; Low Check Standard: 40.0 ± 4.0
	Dissolved Organic Carbon	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	Accuracy (mg/L): High Check Standard: $5.14 \pm 0.9.0$; Low Check Standard: 1.28 ± 0.60
	Alkalinity	At the onset, starting with the initial calibration of instruments for each lake survey, & after the last station on each 12 hour shift	Accuracy (mg/L): High Check Standard: 97-103 (control) or 98-102 (warning); Low Check Standard: 38-42 (control) or 38.5-41.5 (warning)

Table 11-3. Method Performance Criteria - Lab Bias Measures**

Description	Survey Parameter	Minimum Frequency	Performance Criteria
	pH	At the onset, starting with the initial calibration of instruments for each lake survey, & after the last station on each 12 hour shift	Accuracy (SU): High Check Standard: 9.18 ± 0.3 (control) or 9.18 ± 0.2 (warning); Low Check Standard: 6.86 ± 0.3 (control) or 6.86 ± 0.2 (warning)
	Conductivity	At the onset, starting with the initial calibration of instruments for each lake survey, & after the last station on each 12 hour shift	Accuracy ($\mu\text{mhos/cm}$): High Check Standard: 290-297 (control) or 291-296 (warning); Low Check Standard: 193.5-199.5 (control) or 194.5-198.5 (warning)
	Turbidity	At the onset, starting with the initial calibration of instruments for each lake survey, & after the last station on each 12 hour shift	Accuracy (NTU): High Check Standard: 10 ± 2 (control) or 10 ± 1.4 (warning); Low Check Standard: 0.5 ± 0.3 (control) or 0.5 ± 0.2 (warning)
	Total Suspended Solids	Not required but being considered	—
	Benthos Meteorology Phytoplankton Zooplankton	None	—
	Chlorophyll <i>a</i>	Daily	$\pm 10\%$ of true value
	Dissolved Oxygen -Winkler Method	At the beginning of each lake of a regular survey DO surveys: At the beginning & one per shift	± 0.5 mg/L compared to the theoretical

* Interim Limit = These limits will be used until there is enough data to calculate performance limits for this procedure.

** Note: Lab precision also can be monitored from lab check standards by maintaining control charts and calculating the standard deviation of results.

Table 11-4. Method Performance Criteria - Other Bias Measures

Description	Survey Parameter	Minimum Frequency	Performance Criteria
Lab spike into field sample (matrix spike) (Measures accuracy of lab and method procedures in the sample matrix) and other measures for physical parameters as described under performance criteria	Alkalinity Benthos Chloride Chlorophyll <i>a</i> Conductivity Dissolved Organic Carbon Meteorology Nitrate + Nitrite Particulate Organic Carbon pH Phytoplankton Silica Total Suspended Solids Total Dissolved Phosphorus Total Phosphorus Turbidity Zooplankton	None	—
	Particulate Nitrogen Particulate Phosphorus	During each batch or 1 per 40 samples, whichever is more frequent	100% ± 20%
	Wind Speed	Each reading	± 2.0 knots, comparison between multiple instruments
	Wind Direction	Each reading	± 1.5 degree, comparison between multiple instruments
	Barometric Pressure	Each reading	± 2.0 mB, comparison between multiple instruments
	Air Temperature	Each reading	± 0.3°C, comparison between multiple instruments
	Sea Depth	Each reading	± 5%, compared to the SeaBird 911 data and charted soundings
	Sea Temperature	Each reading	± 0.5°C, compared to the SeaBird 911 data

Description	Survey Parameter	Minimum Frequency	Performance Criteria
	Ship's Heading	During river transits by range markers and underway	± 1.5 degrees, compared to GPS generated course over ground
	Ship's Water Speed	During river transits by range markers and underway	± 0.5 knot, compared to GPS generated course over ground
	Ship's Position	Each station	± 10 feet, compared to satellite health messages and visual dockside position

Table 11-5. Method Performance Criteria- Laboratory Contamination Measures

Description	Survey Parameter	Minimum Frequency	Performance Criteria
Reagent Blank (Measures the presence or absence of contamination introduced by laboratory systems, reagents, or processes)	Nitrate + Nitrite	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	0.00 ± 0.03 mg/L
	Particulate Phosphorus Total Dissolved Phosphorus Total Phosphorus	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	0.0 ± 2.0 µg/L
	Chloride	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	0.0 ± 0.2 mg/L
	Silica	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	0.000 ± 0.015 mg/L
	Particulate Organic Carbon	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	≤ 5 µg/L
	Particulate Nitrogen	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	0.00 ± 0.04 mg/L
	Dissolved Organic Carbon	At the beginning & end of each batch or 1 per 40 samples, whichever is more frequent	0.00 ± 0.60 mg/L
	Alkalinity Benthos Chlorophyll <i>a</i> Meteorology pH Phytoplankton Total Suspended Solids Turbidity Zooplankton	None	—

Table 11-6. Method Performance Criteria- Field Contamination Measures

Description	Survey Parameter	Minimum Frequency	Performance Criteria
<p>Field blank-- water for total forms in lake, filters for particulate forms, filtered water for dissolved forms</p> <p>(Measures the presence or absence of contamination introduced in field sampling procedures and includes lab contamination)</p>	Total Suspended Solids	At least once during the sampling of each Great Lake	± 0.2 mg/L
	Nitrate + Nitrite	One per basin	0.00 ± 0.03 mg/L or $< 1/10$ associated field samples conc, whichever is greater
	Particulate Phosphorus Total Dissolved Phosphorus Total Phosphorus	One per basin	0.0 ± 2.0 μ g/L or $< 1/10$ associated field samples conc, whichever is greater
	Chloride	One per basin	0.0 ± 0.2 mg/L or $< 1/10$ associated field samples conc, whichever is greater
	Silica	One per basin	0.000 ± 0.015 mg/L or $< 1/10$ associated field samples conc, whichever is greater
	Particulate Nitrogen	One per basin	0.00 ± 0.04 mg/L or $< 1/10$ associated field samples conc, whichever is greater
	Dissolved Organic Carbon	One per basin	0.00 ± 0.60 mg/L or $< 1/10$ associated field samples conc, whichever is greater
	Alkalinity	One per basin	< 3 mg/L
	Conductivity	One per basin	< 1 μ mho/cm
	Turbidity	One per basin	< 0.15 NTU
	Particulate Organic Carbon	One per basin	≤ 5 μ g/L
	Benthos Meteorology Phytoplankton Zooplankton	None	—
	Chlorophyll <i>a</i>	One per batch	0.00 μ g ± 0.11

12.0 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

All laboratory instrumentation will be assembled and tested before each survey. Testing will consist of checking all control standards on the assembled systems to (1) verify proper concentration, and (2) demonstrate that all analytical systems to be used on the *R/V Lake Guardian* are capable of running within the limits required using the current standards.

After the equipment is installed on the *R/V Lake Guardian*, a series of stations, usually from Saginaw Bay, will be used for shakedown purposes. In most cases, the entire sampling process is implemented during this shakedown. The GLNPO Monitoring Team Lead will use the shakedown process and results to evaluate the procedures and analytical systems to determine the status of equipment and personnel readiness. Corrective actions will be implemented by the Monitoring Team Lead as warranted by specific problems.

Reagent water for use in the onboard laboratory is produced on the ship. Filters in the water system should be changed at least once per year. The super still is equipped with gauges that indicate when the system is working properly. If questions arise regarding the adequacy of the water purification system, the Chief Scientist or shift supervisor is responsible for evaluating the system.

During the cruise, the lead scientist for the functional area onboard ship or in the land-based laboratories will be responsible for implementing preventative and corrective maintenance procedures necessary to preclude instrument down time and produce precise and accurate data that meets the measurement quality objectives listed in this QAPP. Most analytical instrument and equipment manuals have sections dealing with preventative maintenance. These sections will be read by each person operating the equipment. In addition to the recommendations offered by the instrument/equipment manuals, QC samples and calibration requirements for the Survey parameters will be used as an indicator of necessary equipment maintenance (see Table 13-1). Instruments requiring calibration above normal frequency will be identified and evaluated for maintenance.

Preventative procedures also will include inspecting all onboard instruments for worn parts or erratic behavior (as indicated by QC results) after each survey. To prevent equipment mis-uses all EPA, contractor, and grantee staff will be required to follow all operational procedures for each instrument utilized. This assurance is maintained by the development of detailed SOPs (section 4.2.5; training/certification (section 5); adherence to contractor and grantee QA procedures for equipment, glassware, and reagents; and shakedown activities described above.

To prevent instrument downtime during the cruises, GLNPO will maintain an onboard backup recorder, sampler, colorimeter, pump, manifold, tubing supply and small replacement parts. The GLAS contractor and the biology grantee are each responsible for maintaining a complete inventory of the equipment they use on ship as well as a list of frequently used items (including current vendor and catalog number). This inventory and list will be used to refine the list of back up equipment parts needed for each cruise. The GLNPO Chief Scientists are responsible for keeping similar inventories of all other scientific materials needed onboard ship.

Specific records of preventative maintenance inspections, problems, and corrective actions will be documented by the laboratory analysts in instrument log-books maintained on-site in the laboratory. These logbooks will be periodically reviewed by the biology grantee, the GLAS Contractor, or the Limnology Technical Lead and will be available to the GLNPO QA Manager upon request.

In the event that instruments fail and cannot be repaired during the surveys, back up equipment will be

used or ordered. In some cases, the instruments used for back up purposes may differ from those specified in the QAPPs. To the extent feasible, SOPs will be revised during the survey. If such SOP revision is not feasible during the survey, it will be revised immediately after survey conclusion. In any case, all survey staff responsible for using the new equipment will be trained by the senior scientist onboard ship for that functional area to ensure that all staff are using the new equipment and procedures consistently in the absence a documented SOP.

13.0 INSTRUMENT CALIBRATION AND FREQUENCY

Instrument calibration procedures and frequencies vary according to instrument type. Where possible, a multi-point calibration will be used to establish the full range of the instrument before survey samples are analyzed. The frequency of this initial, multi-point calibration varies across methods due to variations in instrument stability and calibration procedures. While some methods, such as those that employ colorimetric detection procedures, require daily calibration of the instrument, other methods, such as those that employ factory calibrated devices, are more stable and require less frequent calibration. All methods involving onboard calibration procedures require that the instrument be calibrated at least once per working shift (e.g., day) during which samples are analyzed. All calibration standards used on board the ship (or by the land-based laboratories) must be certified as to purity, concentration, and authenticity, or prepared from materials of known purity and composition. Instruments, such as the SeaBird CTD or the wind speed indicator are sent to the manufacturer for calibration and are considered stable enough to require such calibration annually or biannually. Detailed instrument calibration procedures and frequencies will be specified in each of the SOPs prepared to support the Water Quality Surveys. Table 13-1 summarizes these requirements.

Table 13-1. Instrument Calibration Procedures and Frequencies

Instrument	Calibration Procedure	Calibration Standard(s)	Frequency
SeaBird CTD	Factory calibrated	Factory standard	annually
Wind Speed and Direction Young Wind Monitor Electric Speed Indicator company	Factory calibrated	Factory standard	when errors are indicated based on comparison
Barometric pressure Belfort Instrument Company barograph Chelsea Boston aneroid barometer R.M. Young, Model 61201	Factory calibrated	Factory standard	barograph and barometer, annually
Secchi disk	not applicable	not applicable	NA
Turner Turbidimeter	Instrument manual	Formazin	shift
YSI Model 35 Conductivity Bridge	Instrument manual	Shunts	When standards indicate calibration is needed. Standards measured prior to first and second lake of each survey. Meter has not required calibration in 5 years.
AB15 and AR15 pH meter	Instrument manual	buffers pH 7 and pH 10	shift
Fisher Accumet pH meter (for determination of alkalinity)	Instrument manual	buffers pH 7 and pH 10	shift
Lachat - total phosphorus and total dissolved phosphorus	Instrument manual	6 concentrations of KH_2PO_4 and a blank	batch
Lachat - NO_2 - NO_3	Instrument manual	6 concentrations of KNO_3 and a blank	batch
Lachat - chloride	Instrument manual	8 concentrations of NaCl and a blank	batch
Lachat - SiO_2	Instrument manual	5 concentrations of commercial silica and a blank	batch
Technicon - DOC analyzer	Instrument manual	Potassium Biphthalate	batch
Flowmeter for zooplankton tow	SOP LG402	Water	At least annually (summer) and if weather is calm, each cruise.

14.0 INSPECTION/ACCEPTANCE REQUIREMENTS FOR SUPPLIES AND CONSUMABLES

Supplies and consumables used during the Water Quality Surveys generally fall into one of the following five areas:

- 1) Supplies used exclusively by contractors and grantees during performance of their contracts and grants. In this case, the contractor/grantee is wholly responsible for inspection and acceptance and assumes responsibility for the quality of those supplies. General requirements regarding such inspection and acceptance are outlined in each contract or grant. Additional requirements regarding the inspection and acceptance of laboratory supplies are described in the GLAS contractor and grantee Quality Management Plans.
- 2) Consumable supplies obtained by either GLNPO, the GLAS contractor, or the biology grantee and used to support the entire Survey operation. The quality of these supplies is managed (inspected and accepted) by the GLNPO Property Officer.
- 3) Consumable supplies obtained by the ship operations contractor to support the entire Survey operation. The quality of these supplies is managed (inspected and accepted) by the Ship Operations Project Officer.
- 4) The quality of food to be consumed onboard ship is inspected by the Chemical Hygiene Officer to ensure that it is properly handled and safe.
- 5) Non-disposable property, such as computers, instruments, etc., that are purchased to support the Water Quality Surveys are inspected and accepted by the Monitoring Team Lead to verify that they are of sufficient quality to meet survey needs.

15.0 REQUIREMENTS FOR ACQUISITION OF NON-DIRECT MEASUREMENT DATA

The sampling and analysis activities conducted during the Water Quality Surveys do not involve the collection of data obtained from non-measurement sources such as computer databases, spreadsheets and programs, and literature files.

16.0 DATA MANAGEMENT

16.1 Field Data Management

The Chief Scientist has primary responsibility for assuring that all data gathered in the survey is documented. Documentation includes raw instrument level printouts, summary bench sheets, and electronic records generated on board ship and in the laboratories. All shipboard-generated strip charts, bench records, and computer printouts are kept in a folder, indexed by station, until the remaining samples are transferred to the land-based laboratories. All raw data are assembled and indexed by parameter, by lake, and by survey leg. Analog charts and digital conversion printouts will be stapled together. Each parameter will be placed in manilla folder and transferred to the GLNPO Chief Scientist for Board Chemistry upon conclusion of the survey. Several parameters are recorded on the ship's log, such as vessel position and weather conditions. This information is described in LG 300, *SOP for Meteorological Data Aboard the R/V Lake Guardian*. These parameters are then recorded on the GLENDa Station Information Field Recording Form at each station visit and entered into the GLENDa database.

During the surveys, sample collection, preparation, preservation, and board chemistry data will be entered into GLENDa using the GLENDa data input tool. To the extent possible, this data entry will be done at the conclusion of each shift, and in all cases, before the end of the cruise. A Data Flow Diagram is provided in Figure 1 of SOP LG101 in the WQS manual and presents the data management process for data collection and data verification for the WQS. Hard-copy Field Information Recording Forms

(Appendix H of the manual) are used to record data as it is being collected during the survey. The data is then entered into the GLENDA shipboard Remote Data Entry Tool. Output files from the Remote Data Entry Tool are created at the end of each survey leg and the Chief Scientist delivers them to the GLENDA Database Manager. If the tool is not functioning properly, the data can be entered into Excel electronic files, which are a soft-copy version of the recording forms in Appendix H, as a back-up to the tool. If this back-up option is used, the data are entered into the Remote Data Entry Tool from these electronic files at GLNPO headquarters or onboard the ship if the Remote Data Entry Tool begins to function during the survey leg. Once the data are in the Remote Data Entry Tool they are uploaded to GLENDA as unverified data upon completion of each survey.

The Chief Scientist is responsible for transferring the original field information recording forms to the QA Team at GLNPO (Marvin Palmer or his designee) for internal quality control checks. The QA Team conducts checks of the recording forms against the data that has been uploaded to GLENDA and addresses any data discrepancies. After completing these checks and resolving all discrepancies, the QA Team transfers the forms to the Environmental Monitoring and Indicators Team for storage in the designated file cabinet at GLNPO. The pertinent Technical Lead conducts a final review of the data and notifies the Database Manager of approval. The Database Manager then finalizes the dataset as Version 1 and makes the data available. For each dataset, the status of this data management process is tracked by the QA Team on the Data Status Tracking Sheet (Appendix N of the WQS manual).

For each staffing period, the Chief Scientist must assure that all data has been collected, analyzed, and entered into the data entry tool. The Chief Scientist must assure that a copy of the hard-copy field information recording forms is made and placed in the onboard designated file cabinet at the end of each survey leg. The Chief Scientist assures that an electronic copy of all soft-copy field information recording forms is made and transferred to the database manager at GLNPO (Ken Klewin) for storage. The Chief Scientist also must assure that SeaBird data files are processed at the end of each survey leg and returned to the database manager for storage. These items are included on the list of Chief Scientist Roles and Responsibilities (Appendix L of the manual). For the bridge data, The Officer in Charge shall be responsible for reviewing the previous watch entries in the Ship's Log, GLENDA Station Information Field Recording Form and the GLENDA database to assure correctness of the data entered. Errors noted shall be corrected immediately.

16.2 GLENDA Data Management

The GLENDA database manager is responsible for collecting all survey data from the Chief Scientists, uploading these data into the GLENDA database, and maintaining the electronic results submitted by the Chief Scientist in its original format for retrieval if necessary. The database manager also is responsible for implementing any database or data entry system modifications necessary to accommodate the unique requirements of the Water Quality Surveys. Once data are uploaded to the database, the Database Manager is responsible for ensuring control and quality of the database, implementing appropriate security and data release procedures, and for facilitating data retrieval and data dissemination to GLNPO staff, contractors, grantees, and members of the scientific community.

A process has been developed for correcting errors identified in verified data in GLENDA and is illustrated in Figure 2 of SOP LG101 in the WQS manual. Once a data error is identified, a Data Discrepancy Form (Appendix P of the manual) is completed and submitted to the Quality Assurance Manager and Database Manager. Data are revised in GLENDA and the revisions are verified as correct by the QA Team. The pertinent Technical Lead also conducts a final review and notifies the Database Manager of approval. The Database Manager then finalizes the dataset as the subsequent version and makes the data available.

17.0 ASSESSMENTS AND RESPONSE ACTIONS

Several types of assessment activities and corresponding response actions have been identified to ensure that data gathering activities in the Water Quality Surveys are conducted as prescribed and to ensure that the measurement quality objectives established in this QAPP and the data quality objectives established by EPA are met. These activities are summarized in Table 17-1 and discussed in greater detail in Sections 17.1 - 17.7 below.

17.1 Surveillance

All data gathering activities are subjected to surveillance activities during the course of sample collection, sample analysis, and data reporting. The Chief Scientist and Shift Supervisors are responsible for monitoring the activities of all sample collection and onboard analysis activities on a daily basis during the surveys. This daily surveillance is intended to ensure that field and lab procedures are being implemented correctly and that all required samples and data elements are being collected. Problems identified are immediately corrected while in the field.

A second level of surveillance monitoring is performed by the Chief Scientists responsible for each functional area. These scientists inspect and evaluate data as it is reported by laboratory staff. Missing data, inconsistencies, or other anomalies are identified and discussed with the Chief Scientist or Shift Supervisor who was onboard ship at the time of collection or with the laboratory analysts responsible for making the measurements.

Finally, the QA manager is responsible for monitoring the quality of all data gathered during the surveys. This surveillance activity is performed when data are reported and serves as a supplement to the surveillance activities described above.

17.2 Peer Review

A formal peer review is conducted on all survey programs every four years to ensure that monitoring strategies identified for the surveys continue to be appropriate, identify the need for new strategies, and ensure that data gathered during the surveys are being gathered, interpreted, and utilized in a scientifically valid manner.

At a more immediate level, 10% of the planktonic diatom measurements made by the biology grantee are subjected to a real-time peer review that is performed by a senior biologist to verify that the analyst is correctly interpreting sample results.

17.3 Quality System Audits

Quality system audits (QSAs) of the data gathering activities and processes will be conducted on a periodic basis to ensure that the data gathered during each survey fulfills GLNPO's programmatic and QA requirements. These QSAs will be scheduled and managed by GLNPO's QA Manager.

17.4 Readiness Reviews

Several types of 'readiness' reviews will be implemented to ensure that the sampling teams, laboratories, and staff are capable of implementing required data gathering activities before the surveys begin. These reviews include:

- 1) The use of on-site audits prior to award of any new laboratory contracts (i.e., the GLAS contract). Such audits will be conducted by the contract Project Officer and/or the GLNPO QA Manager

- 2) Analysis of standard reference materials and calibration standards prior to each survey. These analyses will be conducted by the laboratory staff normally responsible for survey sample analyses. Results will be reviewed by the laboratory manager and the Technical Lead responsible for that functional area.

17.5 Technical Systems Audit

The GLNPO QA Manager, or his designee, will conduct on-site audits of the facilities, equipment, staff, and sample analysis, training, Record keeping, data validation, data management, and data reporting procedures used at the GLAS contract lab, the biology grantee lab, and in the onboard ship labs. These audits will be performed on an annual or biennial basis unless the results of the readiness reviews, data quality audits, and surveillance suggest serious or chronic laboratory problems that warrant more frequent on-site examinations and discussion with laboratory personnel. All technical system audits will be conducted using a standardized audit checklist to facilitate an audit walk-through and document audit findings. At a minimum, audit participants will include the EPA Quality Assurance Manager (or designee). Other auditors may include the Technical Lead, the Environmental Monitoring and Indicators Team Lead, the GLAS Project Officer, the Grant Officer, or contractor QA staff. In such cases, the QA Manager (or designee) staff member will be responsible for leading the audit and conducting a post-audit debriefing to convey significant findings to laboratory staff at the conclusion of the audit. The second staff member will be responsible for gathering pre-audit documentation of problems that necessitated the audit, customizing the audit checklist as necessary to ensure that those problems are addressed during the audit, documenting audit findings on the audit checklist during the audit, and drafting a formal report of audit findings for review by the QAM.

17.6 Data Quality Audits

Data quality audits of survey result files will be performed on a schedule to be jointly determined by the GLNPO QA Manager, the Environmental Monitoring Team Lead, and the Technical Lead of each functional area. These audits will be directed at verifying that data gathered during the surveys meet the MQOs cited in this QAPP and at identifying trends in method and laboratory performance. Individuals responsible for performing these audits, and procedures to be used in performing them, will be determined prior to the next revision of this QAPP.

17.7 Data Quality Assessment

The QA Team Lead for the Surveys, or his designee, will conduct reviews of hard-copy data forms against the data in GLENDa. This review will assess several aspects of data quality including data entry errors, assessments of results against historical data, and evaluation of method performance. The pertinent technical lead also will perform a review and provide final approval of the data to the database manager who will make the data available as version 1 of the data. This process is described in Section 16.1 and illustrated in Figure 1 of SOP LG101 in the Manual. For each dataset, the status of this data quality assessment process is tracked on the Data Status Tracking Sheet (Appendix O of the manual).

Statistical and scientific analyses of the GLENDa database will be performed on a periodic basis to be jointly determined by the GLNPO QA Manager, the Environmental Monitoring Team Lead and the Technical Lead of each functional area. The objective of these analyses is to verify that the data being gathered are suitable for their intended use (water quality monitoring), monitor trends in survey results and water quality to verify that survey objectives of detecting 20% changes in water quality are being met, and identify areas for improvement.

Table 17-1. Assessment and Response Actions

Assessment Measure	Definition	Frequency	Responsible Party	Rationale
Surveillance	Continual or frequent monitoring and verification of the status of an entity and the analysis of records to ensure that specified requirements are being fulfilled	Throughout survey activities, while samples are being analyzed at GLAS laboratory	Chief Scientists during surveys; QA mgr when data are reported	Identify and correct field and lab analytical problems as soon as they occur to prevent problems at future sites or surveys; identify data reporting or QA deficiencies prior to next survey.
Peer Review	A documented critical review of work. Conducted by qualified individuals who are independent, but technically equivalent of those who performed the work.	Performed on 10% of phytoplankton, zooplankton, and benthos determinations Performed on all survey programs every 4 years	GLNPO Peer Review Coordinator	<ul style="list-style-type: none"> • Ensure organism identification and enumeration is activities are technically adequate, competently performed, properly documented, and satisfy established technical and quality requirements. • Ensure data are being correctly interpreted and utilized; identify monitoring strategies that should be modified
Management Systems Review	Qualitative assessment of a data collection operation and/or organization to establish whether the prevailing quality management structure, policies, practices, and procedures are adequate for ensuring that the type and quality of data needed are obtained.	Periodically	QA Manager	Ensure survey practices continue to meet programmatic and QA requirements established by GLNPO
Readiness Review	A systematic documented review of the readiness for the start-up or continued use of a facility, process or activity. Typically conducted before proceeding beyond project milestones and prior to initiation of a major phase of work.	<ul style="list-style-type: none"> • On-site audits prior to award • Analysis of SRMs, calibration standards prior to survey • Collect health records prior to surveys 	<ul style="list-style-type: none"> • Contract PO and GLNPO QAM • Contract or Grantee lab managers • CHO 	<ul style="list-style-type: none"> • Verify contractor or grantee is capable of producing precise and accurate results with the methods they will use during the survey • Verify all survey participants are physically capable of participating in offshore sampling
Technical Systems Audit	A thorough, systematic, on-site, qualitative audit of facilities, equipment, personnel, training, procedures, Record keeping, data validation, data management, and reporting aspects of a system.	Annually or biannually	QA Manager or designee	Ability of each laboratory to adequately analyze and report data will be assessed prior to analysis and continually throughout analyses via other QA/QC measures described in this QAPP.
Audit of Data Quality	Systematic and independent examination to determine if quality activities and related results comply with planned arrangements and whether these arrangements are implemented effectively and are suitable to achieve objectives.	TBD	GLNPO QA Manager	To verify that all data collected meet MQOs established for this study; identify trends in data quality with respect to method and laboratory performance

Assessment Measure	Definition	Frequency	Responsible Party	Rationale
Data Quality Assessment	Statistical and scientific evaluation of the data set to determine the validity and performance of the data collection design and statistical test, and to determine the adequacy of the data set for its intended use.	TBD	Technical Leads/Data Managers	Evaluate overall accuracy and quality of the survey results, identify trends in water quality.

18.0 REPORTS TO MANAGEMENT

The GLNPO Management Committee meets every week to discuss data gathering activities, status, and priorities within the Office. The Environmental Monitoring Team Lead, the QA Team Lead, the Information Management Team Lead, and the Safety Team Lead each are responsible for reporting to this group on a monthly basis.

In addition, GLNPO will submit formal reports of survey activities and findings concerning the Water Quality Surveys as part of GLNPO's annual reporting under the Government Performance Results Act.

19.0 DATA VERIFICATION AND VALIDATION

Data verification activities are performed by GLAS contract managers and the GLAS QC Coordinator before data are submitted to GLNPO. These verification activities include a detailed review of results to identify QC measures that failed to meet the objectives outlined in Section 11 of this QA. Measures failing to meet these objectives will be reviewed carefully to identify the cause of the problem and determine if reanalysis is warranted. In the event that reanalyses is determined to be infeasible (due to expired holding times, lack of sample volume, etc), or not warranted (QC failure is not expected to compromise survey results), the data are submitted with QC flags to indicate the nature of the failure.

Data validation activities are conducted by GLNPO's Technical Lead of each functional area. These data validation activities are conducted using best professional judgement. This judgement reflects in-depth expertise and knowledge of the characteristics of each lake.

20.0 REFERENCES

- [1] *EPA Requirements for Quality Assurance Project Plans*, EPA QA/R-5, EPA Quality Assurance Division, March 2001.
- [2] *EPA Guidance for Quality Assurance Project Plans*, EPA QA/G-5, EPA Office of Research and Development, Washington, D.C. 20460. EPA/600/R-98/018. February 1998.
- [3] Kwiatkowski, 1980. *Regionalization of the Upper Great Lakes with Respect to Surveillance Eutrophication Data*. J. Great Lakes Res 6(1):38-46.
- [4] Lesht, B.M., 1984. *Lake Michigan Eutrophication Model: Calibration, Sensitivity, and Five-Year Hindcast Analysis*. Report ANL/ER-84-3, Environmental Research Division, Argonne National Laboratory, Argonne, IL.
- [5] Moll et al, 1985. *Lake Huron Intensive Survey 1980*. Special Report No. 110. Great Lakes Research Division, University of Michigan, Ann Arbor, MI.
- [6] El-Shaarawi, 1984. *Statistical Assessment of the Great Lakes Surveillance Program, 1966-1981*. National Water Research Institute, Inland Waters Directorate, Scientific Series No. 136.